Detection, Determination and Separation of Metal Ions With Special Reference to Iron, Titanium, Aluminum and Beryllium

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A C K N O W L E D G M E N T

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1. Preparation and Properties of Stannic Molybdate. J. Inorg. Nucl. Chem., (In press).

2. Detection Tests Employing the Tin(IV) Molybdate Exchanger: Detection of Iron. Chemist Analyst, (In Press).

3. Quantitative Separation of Titanium from Numerous Metal Ions and of Iron, Aluminum and Titanium by Paper Chromatography. J. Chromatog., (In Press).

4. A Study of Interferences in the Spectrophotometric Determination of Titanium with Sulfosalicylic Acid. Anal. Chim. Acta., (In Press).

5. Dead Stop Titration of Lead(II) with Potassium Hexacyanoferrate(II) in Presence of Barium. Transactions of SAEST Vol. I, No. 2., 1 (1966).

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A B S T R A C T

Stannic molybdate has been prepared by mixing 0.02M solution of stannic chloride and 0.05M ammonium molybdate in the ratio 5:4 (V/V). The properties, composition and the ion exchange behaviour of this substance have been studied and compared with stannic phosphate. This substance has been used for specific detection of iron (II). The detection limit is 5μg. Stannic molybdate beads turn black in the presence of ferrous ions. No other cation gives this test. The color reactions of stannic molybdate with various organic substances have also been studied.

Chromatography on papers impregnated with stannic molybdate has been performed. Very selective and clean separations of metal ions have been achieved on these papers.

Iron, titanium and aluminum have been separated quantitatively using paper chromatography. The zones are equidistant. The results are reproducible and accurate.

Sulfosalicylic acid has been used for the selective determination of titanium at 355 mμ . The interferences

caused by some cations have been masked with suitable masking agents. Effects of pH, temperature and time on the sulfosalicylic acid complex have been studied.

The dead-stop technique has been used to determine lead in presence of barium using potassium ferrocyanide as titrant. The effect of the variation of voltage has been studied in detail and the titration has been performed at 0.6 volts. Standard deviation for nine experiments is 0.0312.

C H A P T E R I

I N T R O D U C T I O N

Analytical chemistry deals with the problems of separation, detection and determination of the various components in a mixture. Mixtures may be classified as organic or inorganic. Organic compounds are mostly unionised while inorganic substances are more or less ionic in nature. The analytical chemistry of cations has attracted attention more conspicuously than that of the anions. Amongst the cations the group Fe - Al - Ti is particularly difficult to separate. For difficult separations a number of interesting techniques are being used now-a-days: (i) solvent extraction (1,2,3); (ii) Electrophoresis (4,5,6); (iii) Ion exchange (7,8,9) (iv) Chromatography (10,11,12).

Ion exchange is an excellent method of separation for the various ionic materials. This technique is being developed along the following lines: (a) Preparation of new synthetic inorganic ion exchangers (13,14,15,16). (b) Studies of the fundamental properties of these ion

exchangers i.e. K_d values, solubility, ion exchange capacity etc. (c) Impregnation of papers with these ion exchangers and the separation of metal ions on the ion exchange papers (17,18,19,20). (d) The use of ion exchange beads for the detection of metal ions in traces (21).

The preparation of new ion exchangers is important in many respects: (a) By a suitable change in the chemical nature of an ion exchanger it should be possible to find solutions to specific problems (b) By finding the pore sizes of the various ion exchangers one can take advantage of a new technique known as Molecular sieve chromatography (22,23). This technique which is still in its infancy holds considerable promise (c) The data on K_d values for numerous metal ions in various solvents lead to interesting solutions of many complicated problems (d) When one has to detect a very small quantity of an ionic species the resin bead test is the most useful. Most of the work uptil now has however, been on organic resin beads but there is no reason why inorganic ion exchangers can not be used.

After separation has been achieved the next important step is the determination of the various constituents. The methods of determination which are the most common may be classified as: (i) Spectrophotometric methods

(ii) Electrical methods. The spectrophotometric methods are most commonly used because they are simple selective and rapid. However, there is need for continuous improvement in these methods (24,25). Electrical methods on the other hand are not so specific but they are sensitive and their selectivity can be improved by the proper adjustment of pH and by the use of a suitable complex forming agent. Amongst the electrical methods the dead-stop technique is particularly attractive (26,27,28,29). The instrumentation is simple and once the conditions have been established the titration is very easy to perform. This technique may be used with advantage even in those reactions where no color is produced. And therefore the two techniques may be said to complement each other.

The present work was therefore undertaken to prepare a new ion exchange material (Stannic Molybdate) and to study its fundamental properties and its utility in analytical separations. Papers were also impregnated with this ion exchanger and it was found that many difficult and interesting separations are achieved very easily on these papers.

The ion exchange material can be used not only for the separation of various cations but it can also be used for the concentration and detection of metal ions. The

concentration of metal ions has been achieved by a very novel technique i.e. precipitation ion exchange (30). However, since inorganic ion exchange beads have not been used to any considerable extent for the detection of traces of metal ions an effort has been made to develop a new specific test for an important cation (Fe^{++}) based upon reaction with inorganic ion exchange beads.

Partition paper chromatography also offers simple solutions to difficult analytical problems. And despite the fact that thousands of papers have been published in this field significant contributions continue to appear (31,32,33). An attempt was therefore made to study the qualitative separation of Fe - Al - Ti with this technique.

After separation and detection of an ion the next important step is its determination. In this study electrical as well as nonelectrical methods of analysis have been examined for the determination of common ions like titanium and lead. It has been found that new methods of determination for these two ions are significant and they are an improvement over the existing methods of analysis. In the following pages are described the method of approach, the chemistry of the processes involved and the experimental details of these new analytical methods.

The limitations and the advantages of these techniques have been compared with those of the existing procedures.

LITERATURE CITED

1. E. Cerrai and G. Ghersini, Anal. Chim. Acta., 37, 295 (1967).

2. J.A.W. Dalziel and H. Thompson, Analyst, 91, 98(1966).

3. B.B. Scott, ibid, 506 (1966).

4. R.A. Bailey and A. Steger, J. Chromatog., 25, 442 (1966).

5. U. Freimuth and K.H. Kludas, ibid, 23, 333 (1966).

6. K. Bachmann and H. Gorisch, ibid, 23, 336 (1966).

7. F.B. Marti and C.A. Herrero, Anales. real soc. espan. Fis Quim., 62,B, 1171 (1966).

8. F.B. Marti and C.A. Herrero, Chim. Analyt., 48, 602 (1966).

9. F.W.E. Strelow, R. Rethemeyer and C.J.C. Bothma, Anal. Chem., 37, 106 (1965).

10. A.H.I. Ben-Bassat,I. Adato and S. Yariv, Chim. Analyt. 48, 609 (1966).

11. R.A.A. Muzzarelli, Talanta, 14, 85 (1967).

12. M.R. Lanigan and C.A. Bartezak, J. Chromatog., 25, 483 (1966).

13. Y. Inoue, J. Inorg. Nucl. Chem. 26, 2241 (1964).

14. L.O. Mederos ibid, 28, 599 (1966).

15. L.H. Bateale, D.V. Deyck and D. Huys, ibid, 27, 683 (1965).

16. D. Betteridge and G.N. Stradling, ibid, 29, 2652 (1967).

17. J. Sherma, Talanta, 13, 138 (1966).

18. M. Qureshi, I. Akhtar and K.N. Mathur, Anal. Chem., 39, 1768 (1967).

19. M. Qureshi and S.Z. Qureshi, J. Chromatog., 22, 198 (1966).

20. G. Alberti and F. Dobici and G. Grassini, ibid, 8, 103 (1962).

21. N. Fujimoto, Chemist Analyst, 49, 4 (1960).

22. D.N.W. Anderson, I.C.N. Dea, S. Rahman and J.F. Stoddart, Chem. Comm., 145 (1965).

23. A.N. Schwartz, A.W.G. Yee and B.A. Zabin, J. Chromatog., 20, 154 (1965).

24. E.N. Pollock and A.N. Miguel, Anal. Chem., 39, 272 (1967).

25. J.G. Sen Gupta, ibid, 18 (1967).

26. H.L. Kies, J. Electroanal. Chem., 8, 325 (1964).

27. R.B. William and H. Frye, Anal. Chem., 36, 945 (1964).

28. P. Vydra and J. Vorlicek, Talanta, 12, 139 (1965).

29. D. Singh and A. Verma, J. Sci. Res. Banaras Hindu Univ. 14, 44 (1963-64).

30. R.N. Ruch, F. Tera and G.H. Morrison, Anal. Chem., 37, 1565 (1965).

31. S.K. Nath and R.P. Agarwal, Micro. Chem. J., 11, 472 (1966).

32. G.A. Welford, E.L. Chiotis and R.S. Morse, J. Chromatog., 25, 144 (1966).

33. I.M. Hais and K. Macek, "Paper Chromatography, A Comprehensive Treatise", III Edition, Publishing house of Czechoslovak Acad. of Sciences, Prague, (1963).

C H A P T E R II

PREPARATION AND PROPERTIES OF STANNIC MOLYBDATE

The importance of synthetic inorganic exchangers has been recently reviewed (1,2). These materials have found interesting applications in analytical chemistry particularly in the separation of alkali metals and alkaline earths. The emphasis has however been on compounds based upon zirconium. Relatively few fundamental studies have been reported on tin compounds. Inoue (2,3) was the first to study in some detail an inorganic ion exchanger based on tin i.e. stannic phosphate. This material is used for the paper chromatography of metal ions (4,5). However no important studies have been reported on stannic molybdate. Berzelius (6) was the first to prepare this compound but he did not make a detailed study of its properties. This chapter deals with the preparation and ion exchange behaviour of this substance.

E X P E R I M E N T A L

Reagents: Stannic chloride pentahydrate (Poland), ammonium molybdate (Veb Laborchemie Apolda, Germany), sodium molybdate (Riedel, Germany) were used for the gel preparation. For conductometric titrations stannic chloride (Baker Analyzed, U.S.A.) and sodium molybdate (B.D.H. England) were used and stannic chloride was standardized against potassium dichromate (7), using lead for the reduction of tin. All other chemicals were of reagent grade.

Apparatus: High frequency titration was performed on the Sargent Oscillometer Model V (E.H. Sargent and Co., Chicago) in the large cell. Measurements of pH were made on a Philips pH-Meter Model PR 9401. Spectrophotometric work was done on Bausch and Lomb Spectronic-20. Philips conductometer Model (PR 9500) was used for conductometric studies.

Preparation of stannic molybdate: On mixing concentrated aqueous solutions of stannic chloride and ammonium molybdate a white precipitate was formed which on drying gave

a bluish white powder. The properties of this powder have not been investigated further. The stannic molybdate gel was prepared by two methods: (a) by mixing aqueous 0.02M stannic chloride and 0.05M ammonium molybdate in the molar ratio of (1:2); (b) by mixing 0.02M stannic chloride and 0.05M sodium molybdate in the molar ratio of 1:1. The stannic molybdate obtained in (a) or (b) was digested at room temperature for 1-2 hours, washed with water and dried at room temperature. When the gel was immersed in water it broke down easily to small particles with cracking and with slight evolution of heat. These particles were further broken down to the desired particle size in a porcelain mortar and sized by sieving for distribution measurements. To convert it into hydrogen form it was immersed in 1-2M nitric acid for 24 hours with intermittent replacing of the acid; washed several times with water, filtered and dried in air. All studies described in this chapter were made on stannic molybdate prepared by method (a) unless otherwise stated.

R E S U L T S

Composition: 0.3000 grams of the exchanger was dissolved in 10-15 ml of concentrated hydrochloric acid and was diluted with water. Molybdate was precipitated by α-benzoinoxime (8) and weighed as MoO_3 or after dissolving the precipitate in ammonia, molybdenum was reprecipitated as lead molybdate (9) which was dried and weighed. The tin in the filtrate was determined with 0.01M potassium dichromate (7). The molar ratio of Sn:Mo is found to be (1:1) in the sample prepared by method (a) and in the sample prepared by method (b) it is (3:2).

Conductometric studies were made to study the composition. Two ml of 0.1M ammonium molybdate diluted to 100 ml with water were titrated oscillometrically with 0.1N stannic chloride. The resulting curve is given in figure 1. The results of the high frequency titration of sodium molybdate with stannic chloride are shown in figure 2. Direct and reverse conductometric titrations of stannic chloride with sodium molybdate have been found successful (Figures 3 and 4). The apparent combining ratio of Sn:Mo is found to be (2:5).

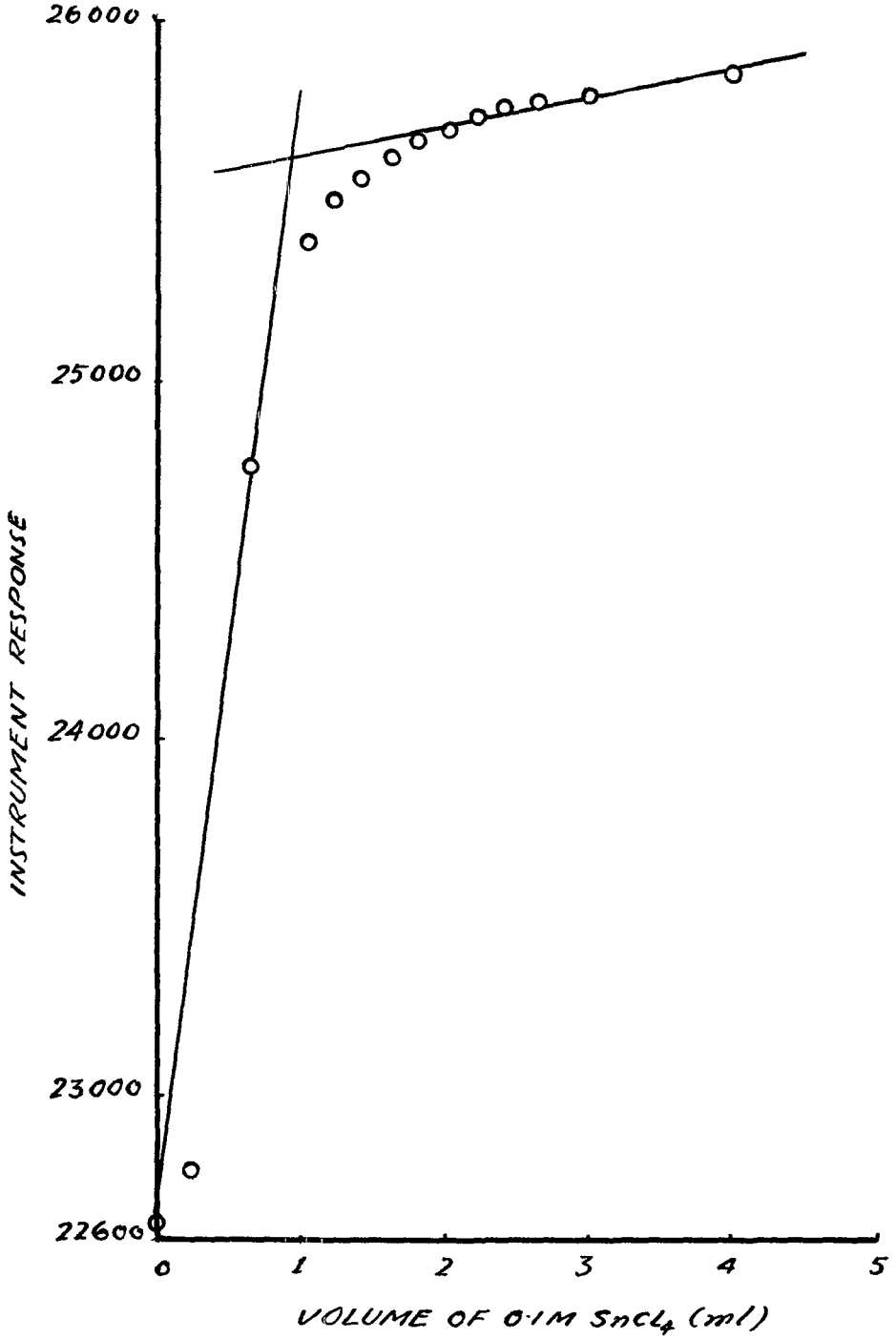


FIG. 1. HIGH FREQUENCY TITRATION OF 2ml OF 0·1M AMMONIUM MOLYBDATE WITH 0·1M. $SnCl_4$

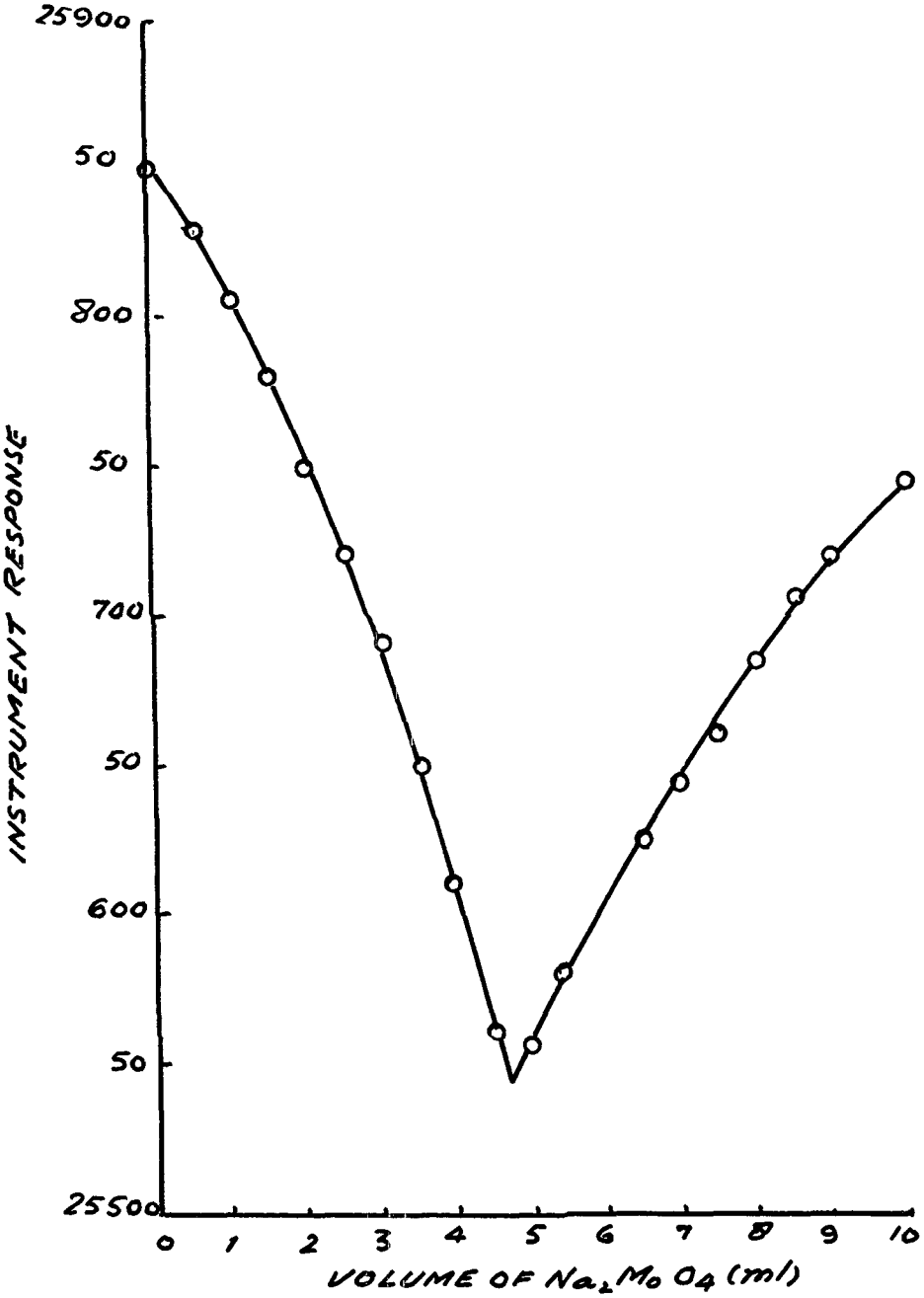


FIG. 2. HIGH FREQUENCY TITRATION OF 2ml 0.096M $SnCl_4$ WITH 0·1M Na_2MoO_4.

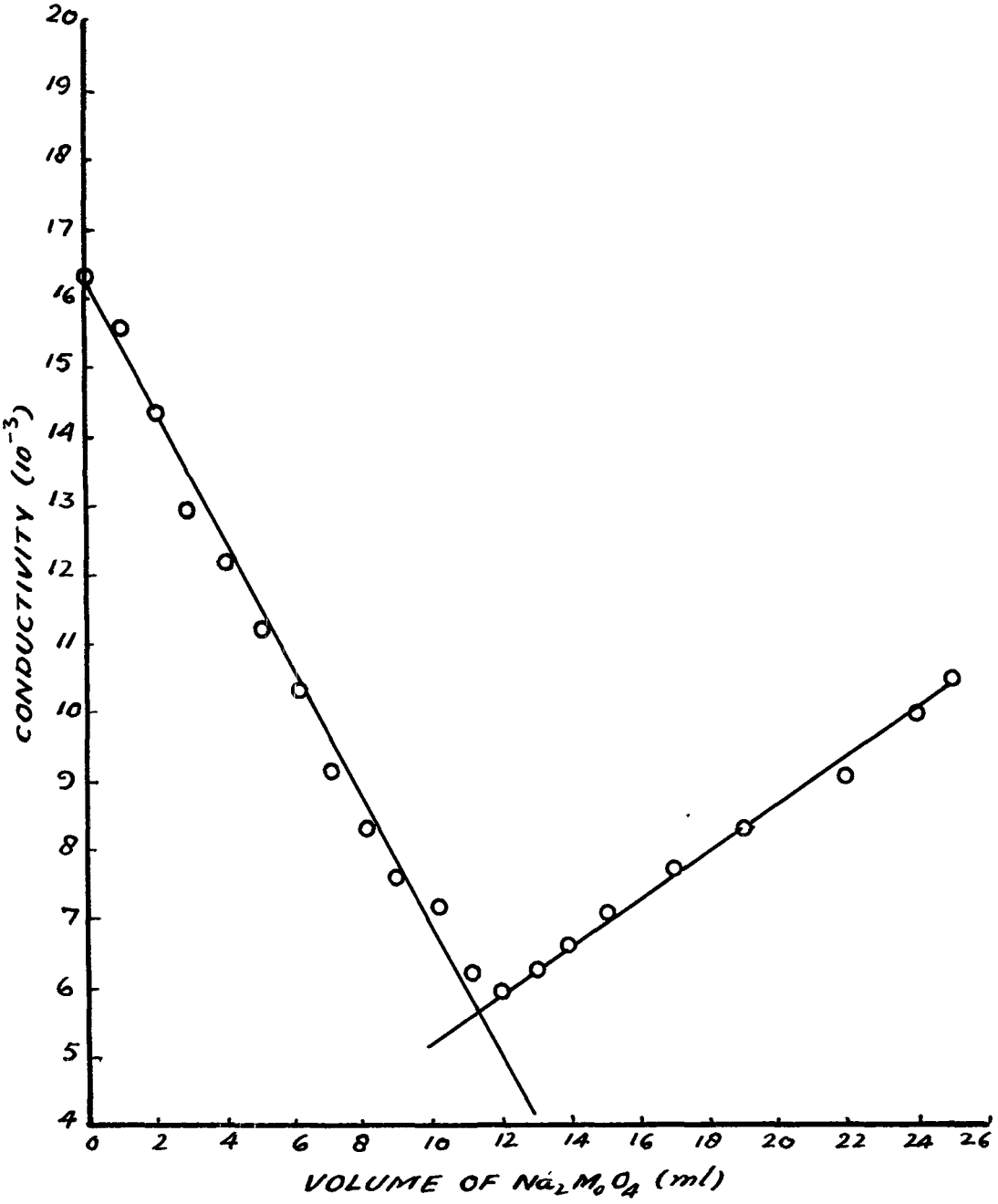
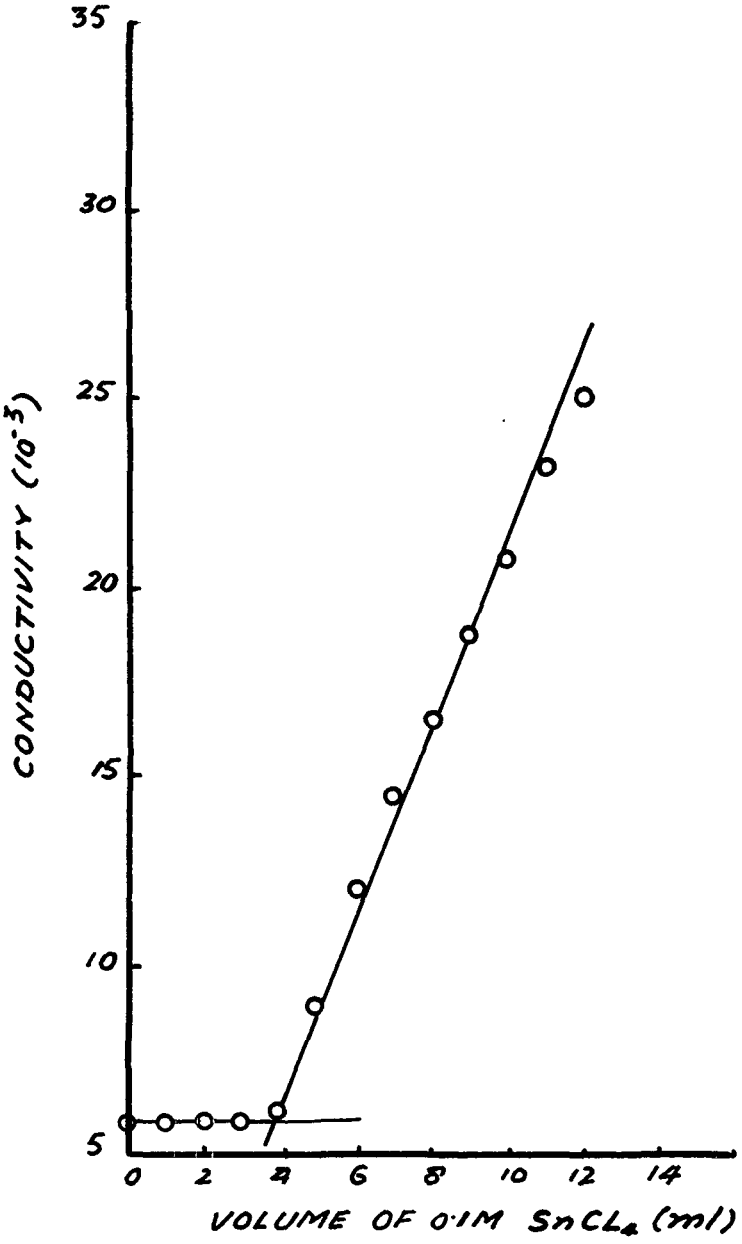


FIG. 3. CONDUCTOMETRIC TITRATION OF 5 ml 0·096 M $SnCl_4$ WITH 0·1 M Na_2MoO_4



4 FIG. 4. CONDUCTOMETRIC TITRATION OF 10 ml 0·1 M Na_2MoO_4 WITH 0·1 M $SnCl_4$

Properties:

(1) Stannic molybdate is in the form of light yellow, hard and semitransparent granules which can be used for column operation. On heating, it turns pale yellow (100°C), greenish yellow (200°C), greenish black (300°C), brownish black (400°C) and finally shining black (600°C). No change in form or color is observed when it is heated in boiling water.

(2) Ion Exchange capacity: The ion exchange capacity was determined by the standard method (10) using some mono- and divalent ions. The results are summarized in table I.

Normal solution of respective salts has been used as eluent and 400 ml. of the effluent has been collected in each case.

T A B L E I

EXCHANGE CAPACITY OF STANNIC MOLYBDATE FOR SOME CATIONS

No.	Exchanging ion	Capacity meq. per dry gram of exchanger
1.	Na^{+}	1.00
2.	K^{+}	0.95
3.	Ba^{++}	1.04
4.	Mg^{++}	0.92

(3) Chemical stability: To get a rough idea of the chemical stability of stannic molybdate in various chemicals, nearly 0.2 - 0.5g of the exchanger was kept in 20 - 50 ml of the solution concerned for 3 days. The substances taken were: hydrochloric, nitric, sulfuric, perchloric, formic, acetic and oxalic acids, sodium hydroxide and ammonia. The behaviour of the exchanger with different substances is as follows:

(i) No change in 3 days: Nitric, sulfuric, acetic, and formic acids of all concentrations, perchloric acid upto 60% and 0.5N HCl.

(ii) No change in one day: In addition to the above: 10% oxalic acid, 10% NH_4OH and 0.02N NaOH.

To study the chemical stability in detail in water and 6N HNO_3 the following procedure was followed.

The exchanger was washed by hot water to remove the influence of tin or molybdenum which may be occluded in the exchanger due to the incompleteness of washing. 500 mg of dry exchanger in H^+ form was refluxed with 50 ml of water or 6N HNO_3 for an hour. After cooling, the

supernatant liquid was filtered through fine filter paper. The filtration was repeated if the filtrate was found turbid. In the filtrate molybdenum was determined by thiocyanate method (11) and tin by phenylfluorone procedure after extraction with diethylammonium diethyl dithiocarbamate (12) spectrophotometrically. The results are given in table II.

T A B L E II

DISSOLUTION OF Mo AND Sn INTO WATER AND 6N HNO_3

No.	Amount dissolved in water		Amount dissolved in 6N HNO_3	
	Sn(mg)	Mo(mg)	Sn(mg)	Mo(mg)
1.	3.500	3.314	9.450	20.250
2.	3.520	3.450	9.675	20.250

(4) Titration curve: The titration curve was determined by the earlier method (13), keeping total sodium ion concentration as 0.1N. The resulting curve is given in figure 5.

(5) Elution curve: The elution curve of the ion exchanger for 0.1M and 1.0N sodium nitrate is

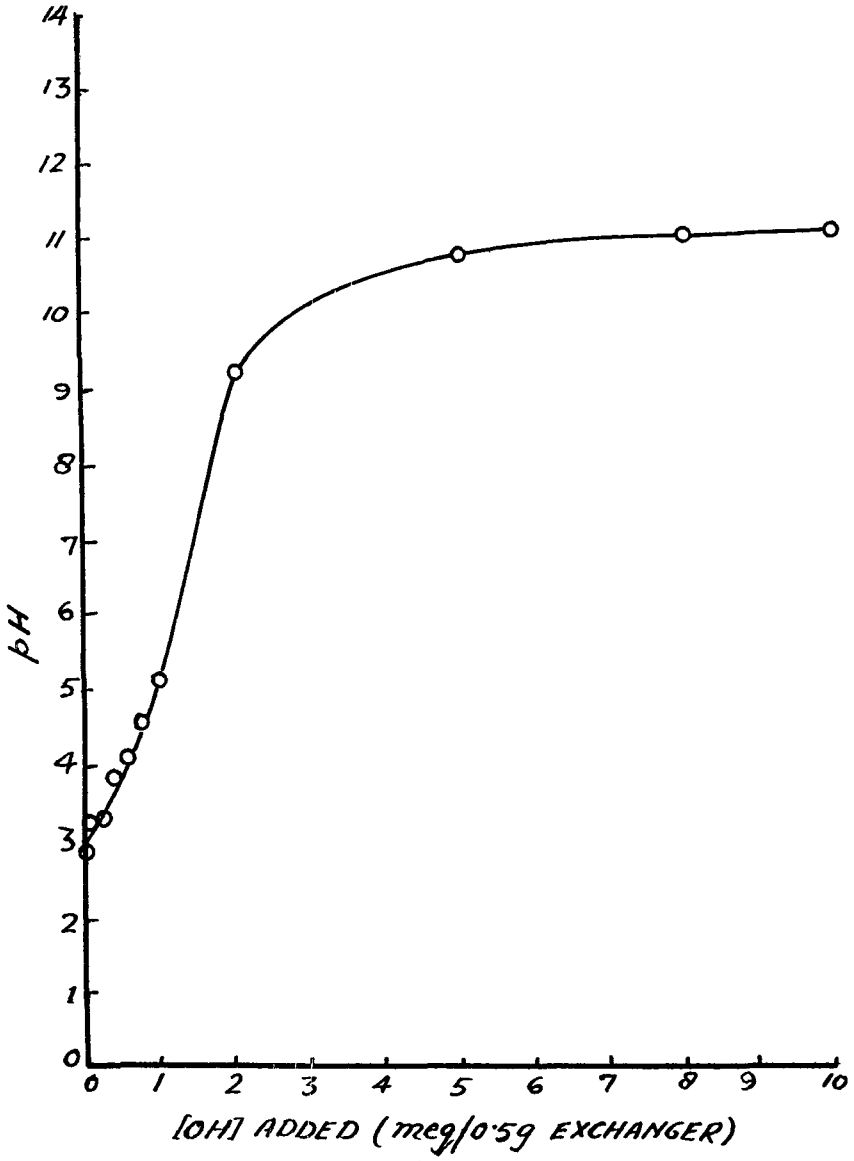


FIG. 5. TITRATION CURVE OF STANNIC MOLYBDATE

shown in figure 6. No further change in the curve was observed when the concentration is increased above 1N (figure 7).

(6) Thermal stability : Heat treatment in air: In order to test the thermal stability of stannic molybdate, 500 mg. of the exchanger dried at room temperature was treated for thermogravimetric analysis at the rate of 3°/minute. The results are summarised in figure 8. The exchange capacity was determined of the samples dried at 100, 200, 300 and 400°C. The results are given in table III.

T A B L E III

EFFECT OF HEAT TREATMENT IN AIR

Sample No.	Drying temperature	Capacity meq/g
1.	Room temperature	1.00
2.	100°C	0.10
3.	200°C	0.07
4.	300°C	0.07
5.	400°C	0.04

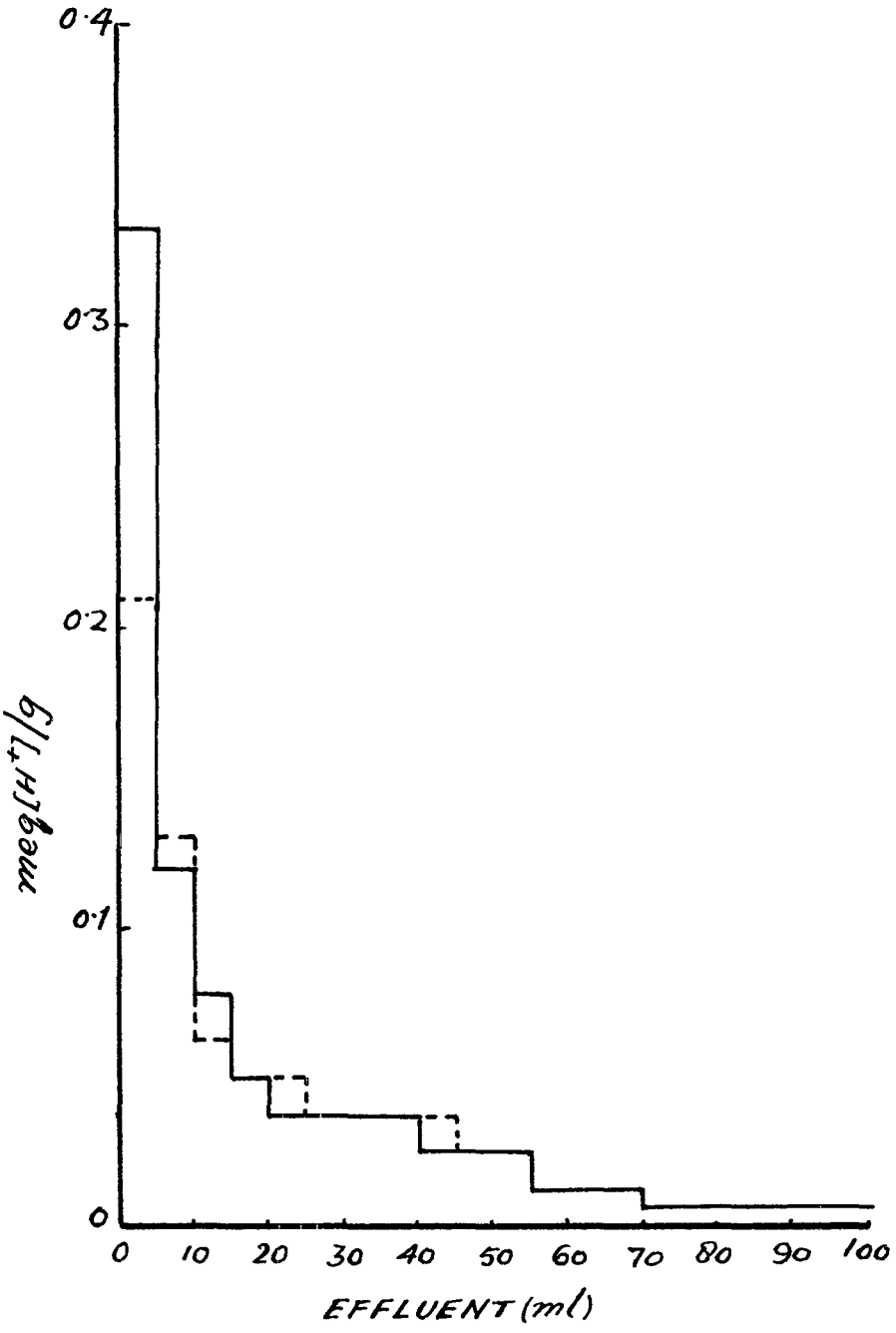


FIG. 6. ELUTION CURVE OF HYDROGENION

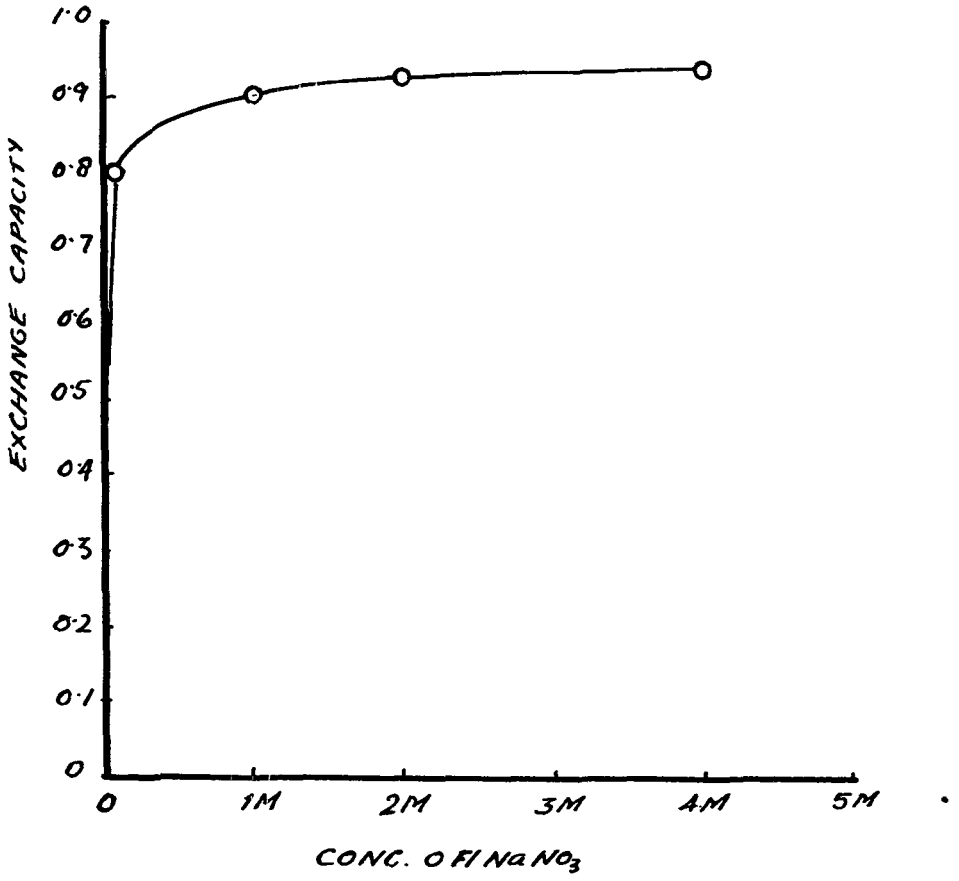


FIG. 7. EXCHANGE CAPACITY AS A FUNCTION OF CONCENTRATION

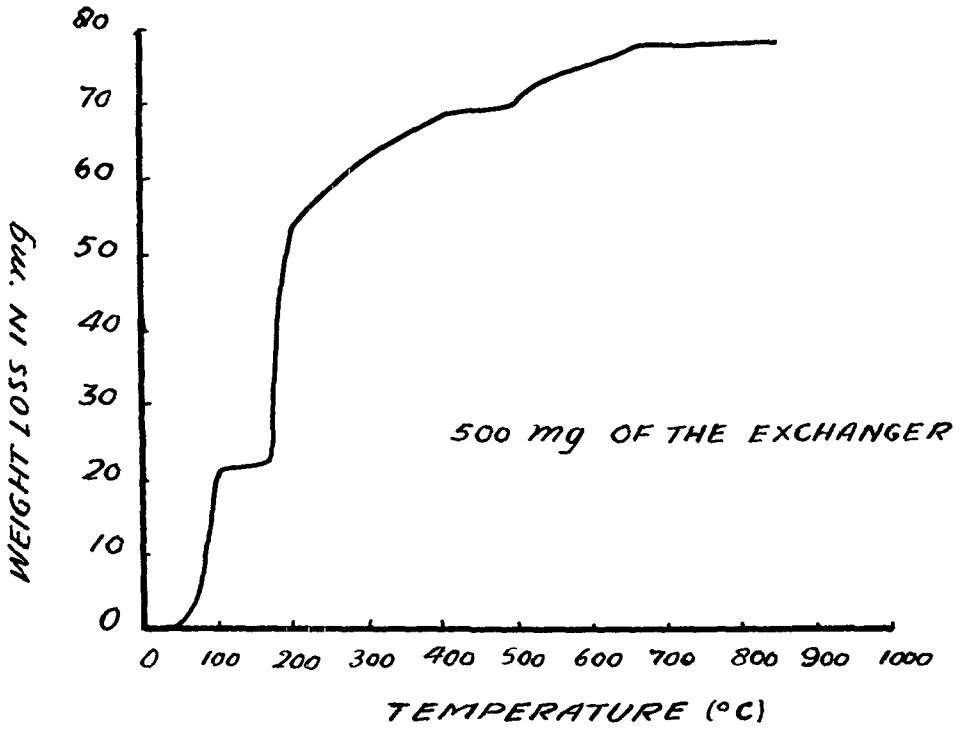


FIG. 8. THERMOGRAM OF STANNIC MOLYBDATE

(7) X-Ray diffraction: To see the crystalline behaviour of the exchanger, stannic molybdate dried at room temperature, 100°C, 200°C, 300°C and 400°C was taken for X-Ray diffraction. All of them were found amorphous to X-Rays.

(8) Distribution coefficients: In order to test the utility of this ion exchanger for separations of analytical interest, the distribution coefficients were determined for numerous metal ions by the method of Inoue (3). Inoue's results on stannic phosphate have also been included for comparison. 500 mg of the exchanger were taken in 10 ml of 10^{-2}M solution in which Kd value is to be determined. The results are given in table IV.

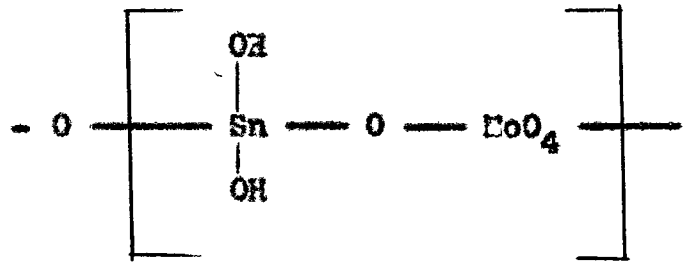
T A B L E IV

DISTRIBUTION COEFFICIENTS OF SOME CATIONS ON STANNIC MOLYBDATE AND STANNIC PHOSPHATE

Cation	Stannic molybdate				Stannic phosphate	
	Compound used	Initial pH	Final pH	Kd value	Compound used	Kd value
Cu(II)	Chloride	5.0	2.5	21.8	nitrate	5870 ± 380
Pd(II)	nitrate	4.5	2.0	285.0	-	-
Y(III)	,,	5.0	2.0	11.0	-	-
Zn(II)	,,	5.0	2.0	15.9	nitrate	315.0±6.6
Ni(II)	Chloride	6.0	2.5	10.3	-	-
Co(II)	nitrate	5.5	2.5	10.0	Chloride	96.70 ± 2.0
Al(III)	,,	4.0	2.5	8.1	-	-
Cd(II)	,,	5.0	2.5	11.3	-	-
Mg(II)	Chloride	5.0	2.5	8.1	-	-
Sr(II)	,,	5.0	2.5	25.7	nitrate	602 ± 11.2
Ba(II)	,,	5.0	2.5	30.0	-	-
Ca(II)	,,	5.0	2.5	20.0	Chloride	2247 ± 121

D I S C U S S I O N

A reference to table IV shows that stannic molybdate has a different selectivity from that of stannic phosphate. Lead has a very high Kd value probably because it forms strong ion pairs with stannic molybdate. It may therefore be possible to separate Pb(II) from its mixture using this exchanger. Quantitative estimations have given the Sn:Mo molar ratio in stannic molybdate as (1:1). Its structure may therefore be tentatively postulated as:



However the (1:1) ratio of Sn to Mo could not be confirmed by high frequency titrations which suggest a ratio of (1:2). These titrations have some interesting aspects. Thus if stannic chloride solution is taken in the titration cell and molybdate solution is added from the burette no end point is observed. The stannic molybdate gel is obtained initially which dissolves on adding

excess of molybdate owing to the possible formation of polymeric substances. However, if the molybdate solution is taken in the titration cell and stannic chloride is added the end point is observed at Mo:Sn ratio (2:1). It is possible that initially $Sn(MoO_4)_2$ is formed which changes to the structure suggested above. Thus it appears that high frequency titration may be very useful for the estimation of Sn^{+4} (for which good methods are not available) but they are not suitable for determining the actual composition of the compound formed. The stannic molybdate gel has also been tested for Cl' and NH_4^+ but no positive test for either of them has been obtained.

The titration curve of stannic molybdate shows one inflection point and therefore probably only one hydrogen ion is affected in the titration and stannic molybdate behaves as a monofunctional acid. Stannic molybdate is hydrolysed significantly in water and the pH of the supernatant liquid on keeping 0.500 grams of stannic molybdate in 50 ml of water for 3 days is 3.8. The color of the supernatant liquid is yellowish. However, when the same experiment is tried in 0.1M NaCl the final pH is 2.9, and the solution is colorless. It appears that the sodium form of the exchanger is more stable than the hydrogen form and the lower pH in this case is due to the combined

effect of hydrolysis and the release of hydrogen ions by the ion exchanger.

The elution curves show that most of the hydrogen ions are released in the first 20 ml of the effluent. The release of hydrogen ions then decreases sharply and finally becomes insignificant after 100 ml. The reaction may be depicted as:

$$\overline{H}^+ + Na^+ \rightleftharpoons \overline{Na}^+ + H^+$$

where $\overline{H}^+$ represents the hydrogen form of the exchanger. Initially the release of hydrogen ions is fast since the whole of the exchanger is in hydrogen form and the forward reaction is fast. As the $[\overline{H}^+]$ decreases the release of H^+ ions becomes slower and it is not of much practical value to continue the elution after 100 ml.

Figure 7 shows that the capacity is strongly dependent on $[Na^+]$ as in the case of stannic phosphate (2). Therefore 1M $NaNO_3$ should be used for elution. Higher concentrations of $NaNO_3$ are not necessary. The capacity of the ion exchanger has been found strongly dependent on drying temperature also. Thus if the ion exchanger has been dried to 100°C the capacity falls to 0.10 meq/gram. This shows that the thermal stability of stannic molybdate is lower than that of stannic phosphate.

A similar behaviour has been noted in the case of zirconium molybdate (1), whose capacity decreased on heating much more than that of zirconium phosphate. By using different monovalent and divalent ions the same capacity has been observed (table I). This shows that the capacity is independent of the exchanged ion and the exchanger can be used for analytical purposes.

On heating the exchanger from 45°C to 100°C there is some loss in weight and a considerable decrease in capacity from 1.0 to 0.1 meq/gram. It therefore appears that significant structural changes take place in this period and condensation of exchanger molecules may occur with removal of water. On heating to 400°C there is loss in weight but not any significant decrease in capacity and only structural water is probably removed. After 400°C the weight becomes almost constant. The X-Ray data do not reveal any crystal structure either at room temperature or at higher temperatures. This behaviour is different from that of stannic phosphate which shows some crystallinity at room temperature and the ion exchanger becomes more and more amorphous as the temperature increases.

LITERATURE CITED

1. C.B. Amphlett, "Inorganic Ion Exchangers", Elsevier publishing Co., N.Y. (1964).

2. Y. Inoue, J. Inorg. Nucl. Chem., 26, 2241 (1964).

3. Y. Inoue, Bull. Chem. Soc. Japan, 36, 1316 (1963).

4. M. Qureshi and S.Z. Qureshi, J. Chromatog., 22, 198 (1966).

5. M. Qureshi, I. Akhter and K.N. Mathur, Anal. Chem., 39, 1766 (1967).

6. J.W. Mellor, "A comprehensive treatise on Inorganic and Theoretical Chemistry", Vol. XI, Longmans Green & Co.,(London), p. 506 (1931).

7. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. III, Interscience publishers Inc. N.Y., pp. 196; 320 (1957).

8. N.H. Furman, "Standard Methods of Chemical Analysis", Vol. I, D. Van Nostrand Co., Inc. Princeton N.J., VI Edn. pp. 675-77 (1963).

9. C. Sterling and W.P. Spuhr, Ind. Engg. Chem. (Anal. Edn.), 12, 33 (1940).

10. O. Samuelson, Diss Tekn. Hogskolan, Stockholm (1944).

11. E.B. Sandell, "Colorimetric Determination of Traces of Metals", III revised Edn., Interscience publishers Inc., N.Y., pp. 649-50 (1959).

12. Ibid, pp. 862-65.

13. H.E. Topp and K.W. Pepper, J. Chem. Soc., Part V, 3299 (1949).

C H A P T E R III

DETECTION OF FERROUS IONS WITH STANNIC MOLYBDATE

Fujimoto (1) has developed sensitive and selective resin spot tests for numerous metal ions. However, synthetic inorganic ion exchangers have not been used for the detection of metal ions. While studying the properties of stannic molybdate (2) it has been found that this compound gives a sensitive test with reducing agents in general. And by a simple modification of the test it has been made selective for ferrous ions.

E X P E R I M E N T A L

Reagents: All chemicals were of reagent grade.

Preparation of beads: The stannic molybdate gel was immersed in water when it broke into small particles. The particles then were crushed and passed through sieves to give beads of 50 - 100 mesh.

Procedure: To one ml of the unknown solution approx. 0.1M $Hg_2(NO_3)_2$ is added dropwise. If a precipitate appears then adding of mercurous nitrate is continued till complete precipitation. The precipitate is filtered and to the filtrate is added 1M aqueous solution of ammonium acetate. Any precipitate appeared is filtered. To this filtrate is added a few beads of the exchanger. The beads turn black in presence of ferrous ions. The detection limit is 5 μg.

R E S U L T S

REACTION OF THE STANNIC MOLYBDATE BEADS WITH INORGANIC IONS

The reactions of the various inorganic cations and anions were studied on beads of stannic molybdate. One milliliter of the reagent solution was added to a few beads of the exchanger and any adsorption on its surface was noted. The results are summarized in tables V and VI. The cations were taken as nitrate, chlorides or sulfates prepared by the method of Elbeih and others (3). For anions the 1M aqueous solutions of sodium, potassium or ammonium salts were used.

T A B L E V

REACTION OF THE EXCHANGER WITH INORGANIC CATIONS

Cations	Color of beads		Cations	Color of beads	
	In cold	On heating		In cold	On heating
Fe^{+2}	B.K. (2 min.)	B.K.	Be^{+2}	-	-
Fe^{+3}	-	Y	Mg^{+2}	-	-
Zr^{+4}	-	-	Ba^{+2}	-	-
Th^{+4}	-	-	Sr^{+2}	-	-
Bi^{+3}	-	-	Ca^{+2}	-	-

TABLE V
(Continued)

Cations	Color of beads		Cations	Color of beads	
	In cold	On heating		In cold	On heating
Sb^{+3}	-	Bl.edges	Sn^{+2}	Br.Bk	D.Bk
Zn^{+2}	-	-	As^{+3}	-	-
Cd^{+2}	-	Y	As^{+5}	-	-
Hg^{+2}	-	-	Tl^{+3}	-	-
Hg_2^{+2}	L.Y.	L.Y.	Tl^{+}	-	-
Pb^{+2}	-	-	V(V)	Y	Y
Cu^{+2}	L.Bl.	Bl.Gr.	V(IV)	L.Bl.	Bl.
Cu^{+}	L.Bl.	L.Gr.	Pd(IV)	O	Y
Ni^{+2}	Gr.	Gr.	La^{+3}	-	-
Co^{+2}	L.P.	P.	Sb^{+5}	-	-
Cr^{+3}	L.Grey	Grey	Y^{+3}	-	-
Pt^{+4}	L.Y.	Y	Ti(IV)	-	-
UO_2^{+2}	Y	Y	Ti(III)	V.Bk.	V.Bk.
Al^{+3}	-	-	W(VI)	-	-
Mn^{+2}	O.	O.	Se(IV)	-	-
Ag^{+}	-	-	Te(IV)	-	-
Ce^{+3}	L.Gr.	Gr.	Na^{+}	-	-
			K^{+}	-	-
			NH_4^{+}	-	-

T A B L E VI

REACTION OF THE EXCHANGER WITH INORGANIC ANIONS

Anions	Color of the beads in 5 min.	10 min.	12hrs.	Anions	Color of the beads in 5 min.	10 min.	12 hrs.
S^{-2}	-	-	Grey	PO_4^{-3}	-	-	-
F^-	-	-	-	CN^-	-	-	-
$S_2O_3^{-2}$	-	P.S.	Br.B & S	Citrate	-	-	-
CH_3COO^-	-	-	-	Nitrate	-	-	-
Cl^-	-	-	-	Nitrite	-	-	-
Br^-	-	-	-	CrO_4^{-2}	L.Y.	Y	Y
I^-	-	-	Bk	$Cr_2O_7^{-2}$	Y	Y	Y
SO_4^{-2}	-	-	-	CO_3^{-2}	-	-	-
BrO_3^-	-	-	-	$Fe(CN^{-4})_6$	L.Br.	Br.	Bk.
ClO_3^-	-	-	-	$Fe(CN)_6^{-3}$	O	O	Br.Bk
tartrate	-	-	-	IO_3^-	-	-	-
Oxalate	-	-	-	CNS^-	-	L.Y.	Y

Abbreviations used in table V and VI.

B	= bead	S	= solution
Y	= Yellow	O	= Orange
L	= light	Gr	= Green
D	= Deep	V	= Violet
Br	= Brown	-	= colorless
Bl	= Blue	Bk	= Black
		P.	= Pink

Reaction of Fe^{+2} at different pH values:

In order to make the test specific for ferrous ions the reaction of ferrous ammonium sulfate solution was studied at different pH values. The pH value was lowered by adding dilute H_2SO_4. The results are summarized in table VII.

T A B L E VII

REACTION OF Fe^{+2} AT DIFFERENT pH VALUES

pH value	Color of beads changes in		
	2 min.	3 min.	10 min.
5.5	Blackish	Black	Black
5.0	,,	,,	,,
4.0	,,	,,	,,
3.0	,,	Blackish	,,
2.0	Colorless	Grey	,,
1.0	,,	Colorless	Blackish

Studies of the Black adsorption with Sn^{+2}, Fe^{+2} and Ti(III) in presence of some useful reagents

In order to make the test specific the test was performed after treatment with some reagents so that the interference of Sn^{+2} and Ti(III) may be removed. The results are summarized in table VIII.

T A B L E VIII

TEST WITH STANNIC MOLYBDATE AFTER TREATING WITH SOME USEFUL REAGENTS

Name of the reagent	Fe^{+2}	Sn^{+2}	Ti^{+3}
Potassium iodide	+	+	+
EDTA	-	Sl. Brown	-
Phosphate	ppt. filter Filtrate gave (-) test.	+	Greyish
Thiourea	-	+	+
Amm. Acetate	+(2 min.)	+	-
Mercurous nitrate	+	Black ppt. filtrate gave (-) test.	White ppt. filtrate gave (-) test.

Reaction of stannic molybdate with organic substances:

When 3 - 4 drops of the following substances were applied to a few beads of the exchanger, no color was obtained either in cold or on heating.

Alcohols: Isoamyl alcohol and octyl alcohol.

Hydrocarbons: Petroleum ether, benzene, and toluene.

Aldehydes: Benzaldehyde, salicylaldehyde, anisaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde and dimethyl aminobenzaldehyde.

Esters: Ethylacetate, methylacetate, diethyloxalate, diethylmalonate, ethylmalonate, ethylacetoacetate, and ethylcyanoacetate.

Ethers: Anisole, dioxan, ether, and isopropyl ether.

Ketones: Acetone, methyl-iso-butyl ketone, ethyl methyl ketone, acetophenone , di-iso-butyl ketone, and cyclohexanone.

Acids: Acetic acid, propionic acid, butyric acid, isobutyric acid, acetic anhydride, benzoic acid, and aqueous solutions of : citric acid, tartaric acid, phthalic anhydride, salicylic acid, cinnamic acid, oxalic acid and malic acid.

Amines: Methylamine (30%), pyridine, diethylaniline, and triethylamine.

Amides: Formamide and aqueous solutions of : acetanilide, nicotinamide, butaramide and chloracetamide.

Carbohydrates: Aqueous solutions of: mannitol, cellobiose, lactose and cellulose.

Following substances gave no adsorption in cold but gave black adsorption on heating:

Alcohols: Methanol, ethanol, n-propanol, n-butanol, allyl alcohol and isopropanol.

Aldehydes: Formaldehyde, acetaldehyde and crotonaldehyde.

Acids: Aqueous ascorbic acid.

Hydrazines: Phenylhydrazine and semicarbazide.

Carbohydrates: Aqueous solutions of: glucose, fructose and sucrose.

The beads turned blue on heating with formic acid while they turned black in the presence of hydrazine hydrate in cold.

D I S C U S S I O N

Stannic molybdate appears to be sensitive and selective for ferrous ions. No other cation gives this test. A number of unknowns have been run containing Fe^{+3}. In none of these Fe^{+2} was detected. It therefore appears that the mercurous nitrate treatment does not reduce Fe^{+3} sufficiently to give a test with stannic molybdate. However, if to the Fe^{+3} solution a little HCl is added followed by excess of zinc metal, then the test solution on decantation gives a positive test with stannic molybdate. It is possible that molybdenum is reduced by the ferrous ions to a black substance containing molybdenum in the lower valence state. Color intensity increases with pH when the pH is increased from 1 to 5.5 (table VII).

In the case of ferrous solution the sensitivity has been found 5 μg in 0.1 ml (4 drops). It is possible to detect even smaller amount of Fe^{+2} by taking one drop (0.025 ml) of the test solution and then 1.25 μg of Fe^{+2} can be detected.

LITERATURE CITED

1. M. Fujimoto, Chemist Analyst, 49, 4 (1960).

2. M. Qureshi and J.P. Rawat, J. Inorg. Nucl. Chem. (In press).

3. I.I.M. Elbeih, J.F.V. McOmie and P.H. Pollard, Diss. Faraday. Soc., 7, 183 (1949).

C H A P T E R IV

SPECIFIC SEPARATION OF GALLIUM, GOLD AND MAGNESIUM AND SEPARATION OF Be - Al - Ga ON STANNIC MOLYBDATE PAPERS

Papers impregnated with ion exchangers combine the advantages of ion exchange, adsorption and partition. Such papers are therefore particularly useful in difficult separations. The separations achieved in this manner are rapid, selective and clean with the discovery of inorganic ion exchangers the value of such papers has increased considerably. Now it is possible to prepare the papers very easily in the laboratory (1-4) and the concentration as well as the nature of the ion exchanger can be varied at will. For these reasons a systematic study of such papers needs particular attention. Lederer et al (5) have described some interesting studies on zirconium phosphate papers showing the effect of pH, nature of the acid used in the eluent, concentration of the exchanger on the paper etc. Recently a systematic study was reported on stannic phosphate and stannic tungstate papers (6). This study showed that these papers are very selective, difficult separations can be achieved very easily and the time required to achieve clean

separations is very short i.e. about 40 minutes. However no such study has been reported on stannic molybdate papers. The present chapter deals with the chromatography of numerous metal ions on these papers.

E X P E R I M E N T A L

Apparatus: Chromatography was performed on Whatman No. 1 paper strips of size 14 by 3 cm. using 20 by 5 cms. glass jars.

Reagents: Chemicals and solvents were either E. Merck (Darmstadt) or B.D.H. Analar grade. Stannic chloride pentahydrate (Poland) and sodium molybdate Riedel (Germany) were used.

Preparation of ion exchange papers: Aqueous solutions of stannic chloride (0.25M) and sodium molybdate (0.25M) were prepared. Paper strips of required size were first impregnated in stannic chloride solution for 3-5 seconds. The excess of the reagent was removed by placing the strips over a filter paper sheet and allowed to dry for 15 minutes at room temperature. The strips were then dipped into sodium molybdate solution for 5 seconds, the excess solution drained off and the strips were placed over a filter sheet. These strips were dried at room temperature and then washed with distilled water in order to remove the excess of the reagents. Finally these were dried at room temperature and used as such for chromatography.

Test solutions: 0.1M solutions of chlorides, nitrates or sulfates of most of the cations were prepared in 0.1N solution of the corresponding acids. Platinum wire was dissolved in aqua regia and diluted with water to give 0.1% solution of platinum. 0.1M antimony and bismuth chlorides were prepared in 30%V/V and 3.7N HCl solutions respectively. 1% solutions of gold and gallium chlorides were prepared in 4N HCl solution and 1% niobium pentachloride was prepared in 10% tartaric acid. 0.1M sodium tungstate, sodium molybdate, potassium chloride, caesium chloride and rubidium chloride were prepared in distilled water. Selenium dioxide was dissolved in water and made alkaline with 1N KOH. 0.1M tellurium solution was prepared by heating tellurium metal with conc. HNO_3 till the residue became white and dissolving in 1N KOH. 0.1M ceric sulfate was prepared in 3.6N H_2SO_4. A 1% titanium solution was prepared by diluting Analar grade titanic chloride with HCl and water. The valencies of the cations used are as follows unless otherwise mentioned: Ag(I), Pb(II), Hg(II), Tl(I), Bi(III), Cd(II), Pd(II), Sb(III), Fe(III), V(IV), Cu(II), UO_2(II), Cr(III), Mn(II), Zn(II), Y(III), Zr(IV), Th(IV), Ce(IV), La(III), In(III), Nb(V), Ca(II), Hf(IV), Ti(IV), Al(III), Be(II), Ga(III), Pt(IV), Se(IV), Te(IV), W(VI), Ir(IV), Au(III), Ru(III), Ba(II), Sr(II), K(I), Rb(I), Cs(I), Mg(II), As(III), Co(II), and Ni(II).

Detectors: Ag, Pb, Hg(I), Hg, Tl, Bi, Cd, Pd, Sb and As zones were detected with yellow ammonium sulfide solution; Fe, V, Cu and UO_2 by aqueous $K_4Fe(CN)_6$ solution. 1% Alcoholic diphenylcarbazide was used to detect the Cr, Mn and Zn spots and 0.1% alcoholic Alizarine Red-S for Y, Zr, Th, Ce(III), Ce, La, In, Nb, Ca, Hf and Ti spots. Al, Be and Ga were detected with alcoholic aluminon solution. A fresh solution of sodium cobaltinitrite was used to detect K, Rb and Cs and stannous chloride in 4M HCl for Pt, Se, Te, W and Ir. Au was detected by 1% alcoholic hydroquinone. 2% Thiourea in 2N HCl was used to detect Ru. A fresh aqueous sodium rhodizonate in neutral medium was used to detect Ba and Sr. Alcoholic Quinalizarine and aqueous $K_3Fe(CN)_6$ were used to detect Mg and Fe(II) respectively. Co and Ni were detected with 1% alcoholic dimethylglyoxime.

Procedure: 1-2 spots of test solutions were spotted with the help of thin glass capilaries. The paper was allowed for 15 minutes conditioning and the solvent was then allowed to ascend (always 11 cms). The front limit (R_L) and the rear limit (R_T) is measured.

R E S U L T S

The results of a study of 47 cations in 11 solvent systems are summarized in table IX.

T A B L E IX

Rf VALUES OF METAL IONS IN SOME SOLVENT SYSTEMS

Cation \ Solvent	1		2		3		4	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Te	0.00	0.00	0.32	0.00	0.00	0.00	0.82	0.00
W	-	-	0.00	0.00	0.36	0.00	1.00	0.00
Ir	-	-	0.42	0.00	-	-	0.00	0.00
Au	0.65	0.00	1.00	0.73	0.00	0.00	1.00	0.76
Ru	1.00	0.00	0.28	0.00	0.31	0.12	0.73	0.00
Ba	1.00	0.86	0.20	0.06	-	-	0.00	0.00
Sr	1.00	0.96	0.20	0.06	0.34	0.16	0.00	0.00
K	-	-	0.31	0.22	0.00	0.00	0.00	0.00
Rb	0.91	0.63	0.30	0.10	0.00	0.00	0.00	0.00
Cs	0.94	0.63	0.30	0.00	0.00	0.00	0.00	0.00
Mg	1.00	0.92	0.32	0.09	0.23	0.10	1.00	0.40
Fe(II)	1.00	0.00	0.71	0.31	1.00	0.91	0.77, 0.00	0.41, 0.00
As	0.80	0.20	0.60	0.00	0.68	0.47	1.00	0.00
Co	1.00	0.80	0.24	0.06	0.41	0.33	0.17	0.08
Ni	1.00	0.82	0.33	0.13	0.20	0.09	0.00	0.00

TABLE IX
(Continued)

Cation \ Solvent	1		2		3		4	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Ag	0.81	0.00	0.00	0.00	0.22	0.00	0.36	0.00
Pb	0.82	0.42	0.40	0.00	0.24	0.00	0.54	0.00
Hg(I)	0.38	0.00	0.00	0.00	0.34	0.00	0.50	0.00
Hg	0.70	0.54	0.68	0.61	0.95	0.82	0.92	0.72
Tl	0.46	0.00	0.28	0.00	0.00	0.00	0.00	0.00
Bi	0.91	0.00	0.64	0.40	0.34	0.10	0.70	0.36
Cd	0.74	0.69	0.68	0.60	0.60	0.40	0.56	0.48
Pd	0.98	0.62	0.54	0.00	0.22	0.04	0.68	0.43
Sb	0.08	0.00	0.68	0.38	0.80	0.54	-	-
Fe	1.00	0.00	0.67	0.60	1.00	0.91	1.00	0.00
V	1.00	0.90	0.31	0.15	0.13	0.02	0.54	0.00
Cu	0.93	0.88	0.45	0.27	0.54	0.33	0.78	0.33
UO_2	1.00	0.80	0.51	0.27	0.57	0.34	0.77	0.33
Cr	0.95	0.83	0.45	0.00	0.20	0.06	0.09	0.00
Mn	-	-	0.37	0.18	0.23	0.12	0.10	0.02
Zn	-	-	0.58	0.48	0.73	0.62	0.74	0.48
Y	0.99	0.88	0.22	0.10	0.00	0.00	0.00	0.00
Zr	0.16	0.00	0.20	0.00	0.04	0.00	0.00	0.00
Th	0.90	0.55	0.20	0.04	0.09	0.00	0.36	0.00
Ce(III)	0.95	0.81	0.20	0.07	0.00	0.00	0.00	0.00

T A B L E IX
(Continued)

Cation \ Solvente	1		2		3		4	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Ce	0.99	0.90	0.20	0.06	0.00	0.00	0.00	0.00
La	1.00	0.94	0.20	0.10	0.00	0.00	-	-
In	1.00	0.93	0.68	0.40	0.46	0.30	0.63	0.45
Nb	-	-	0.50	0.20	0.00	0.00	0.59	0.00
Ca	1.00	0.91	0.29	0.14	0.14	0.02	0.00	0.00
Hf	0.20	0.00	0.09	0.00	0.09	0.00	0.00	0.00
Ti	0.45	0.00	0.22	0.00	0.38	0.00	0.09	0.00
Al	1.00	0.92	0.32	0.14	0.18	0.06	0.00	0.00
Be	1.00	0.91	0.52	0.31	0.45	0.35	0.11	0.01
Ga	1.00	0.92	0.70	0.60	1.00	0.91	0.95	0.77
Pt	0.80	0.00	0.70	0.60	-	-	0.63	0.40
Se	0.08	0.00	0.10	0.00	0.31	0.00	1.00	0.00

T A B L E IX
(Continued)

Cation	Solvents 5		6		7		8	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Te	0.00	0.00	0.00	0.00	0.00	0.00	-	-
W	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00
Ir	0.00	0.00	-	-	0.14	0.00	0.00	0.00
Au	1.00	0.84	1.00	0.86	0.54	0.32	1.00	0.77
Ru	0.46	0.00	0.24	0.00	1.00	0.00	0.60	0.00
Ba	0.15	0.03	0.22	0.00	1.00	0.92	0.00	0.00
Sr	0.30	0.13	0.00	0.00	1.00	0.90	0.00	0.00
K	0.32	0.21	0.46	0.22	-	-	0.00	0.00
Rb	0.33	0.20	0.42	0.28	-	-	0.00	0.00
Cs	0.32	0.21	0.38	0.20	0.98	0.80	0.00	0.00
Mg	0.31	0.18	0.36	0.22	1.00	0.94	0.00	0.00
Fe(II)	0.18	0.00	0.31	0.00	1.00	0.00	0.63	0.50
As	0.91	0.42	-	-	0.60	0.00	1.00	0.00
Co	0.22	0.10	0.32	0.18	1.00	0.92	0.23	0.15
Ni	0.33	0.10	0.34	0.17	1.00	0.81	0.10	0.00
Ag	0.00	0.00	0.21	0.00	0.00	0.00	0.51	0.00
Pb	0.08	0.00	0.20	0.10	0.95	0.50	0.40	0.00
Hg(I)	0.00	0.00	0.80	0.00	0.00	0.00	0.86	0.00
Hg	0.81	0.43	0.85	0.53	1.00	0.85	0.92	0.71
Tl	0.00	0.00	0.02	0.18	0.60	0.00	0.00	0.00
Bi	0.66	0.15	0.73	0.46	1.00	0.92	0.70	0.54

TABLE IX
(Continued)

Cation	Solvents 5		6		7		8	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Cd	0.34	0.25	0.41	0.20	1.00	0.94	0.45	0.40
Pd	0.58	0.04	0.82	0.35	1.00	0.79	0.63	0.45
Sb	0.21	0.00	0.22	0.00	0.08	0.00	0.81	0.54
Fe	0.10	0.00	0.24	0.00	0.91	0.00	0.80	0.50
V	0.24	0.00	0.43	0.14	0.94	0.88	0.28	0.02
Cu	0.31	0.00	0.36	0.00	1.00	0.98	0.40	0.31
UO_2	0.58	0.29	0.78	0.54	0.95	0.85	0.77	0.31
Cr	0.22	0.00	0.32	0.18	0.98	0.84	0.09	0.00
Mn	0.26	0.14	0.40	0.25	0.96	0.83	0.14	0.03
Zn	0.50	0.29	0.39	0.20	1.00	0.92	0.76	0.54
Y	0.18	0.00	0.32	0.14	0.98	0.82	0.00	0.00
Zr	0.62	0.00	0.28	0.00	0.13	0.00	0.00	0.00
Th	0.00	0.00	0.42	0.00	-	-	0.34	0.00
Ce(III)	0.18	0.00	0.30	0.18	0.94	0.83	0.00	0.00
Ce	0.91	0.72	0.30	0.00	0.00	0.00	0.00	0.00
La	0.20	0.00	0.30	0.13	1.00 0.00	0.86 0.00	0.00	0.00
In	0.14	0.00	0.58	0.32	1.00	0.00	0.68 0.00	0.54 0.00
Nb	0.20	0.00	0.00	0.00	-	-	0.60	0.00
Ca	0.32	0.13	0.41	0.27	1.00	0.96	0.36	0.00

T A B L E IX
(Continued)

Cation	Solvents 5		6		7		8	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Hf	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00
Ti	0.00	0.00	0.18	0.00	0.88	0.00	0.05	0.00
Al	0.34	0.10	0.40	0.10	1.00	0.96	0.00	0.00
Be	0.45	0.29	0.65	0.46	1.00	0.94	0.18	0.05
Os	0.42	0.00	0.42	0.20	1.00	0.96	0.92	0.77
Pt	0.00	0.00	0.58	0.00	0.95	0.68	0.77	0.68
Se	0.00	0.00	0.00	0.00	0.13	0.00	-	-

TABLE IX
(Continued)

Cation	Solvents 9		10		11	
	R_L	R_T	R_L	R_T	R_L	R_T
Te	0.13	0.00	0.82	0.64	0.61	0.00
V	0.40	0.00	0.40	0.00	0.30	0.00
Ir	1.00	0.00	-	-	-	-
Au	0.60	0.36	1.00	0.89	1.00	0.86
Ru	0.00 1.00	0.00 0.00	0.70	0.00	0.90	0.00
Ba	1.00	0.89	0.55	0.20	0.00	0.00
Sr	1.00	0.90	0.45	0.21	0.00	0.00
K	1.00	0.86	0.60	0.32	0.00	0.00
Rb	0.95	0.81	0.64	0.45	0.00	0.00
Cs	1.00	0.83	0.14	0.00	0.05	0.00
Hg	0.00	0.00	1.00	0.90	1.00	0.00
Fe(II)	-	-	0.91	0.80	0.70	0.27
As	1.00	0.00	1.00	0.00	1.00	0.00
Co	1.00	0.90	0.64	0.45	0.32	0.18
Ni	1.00	0.68	0.77	0.52	0.00	0.00
Ag	0.00	0.00	0.27	0.00	0.50	0.00
Pb	0.77	0.36	-	-	0.32	0.00
Hg(I)	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	-	-	0.90	0.73
Tl	0.00	0.00	0.00	0.00	0.00	0.00
Bi	1.00	0.93	0.93	0.65	0.80	0.56
Cd	1.00	0.92	0.90	0.80	-	-

T A B L E IX
(Continued)

Cation	Solvents 9 R_L	9 R_T	10 R_L	10 R_T	11 R_L	11 R_T
Pd	1.00	0.90	0.90	0.77	0.85	0.45
Sb	0.00	0.00	1.00	0.89	-	-
Fe	0.92	0.00	0.85	0.76	0.78	0.00
V	-	-	0.88	0.64	0.18	0.00
Cu	1.00	0.85	0.70	0.54	0.44	0.24
UO_2	1.00	0.92	0.77	0.57	0.75	0.27
Cr	1.00	0.93	0.73	0.50	0.05	0.00
Mn	1.00	0.96	0.68	0.36	0.22	0.04
Zn	1.00	0.90	0.96	0.86	0.90	0.70
Y	-	-	0.50	0.00	0.00	0.00
Zr	0.00	0.00	0.32	0.00	0.16	0.00
Th	1.00	0.00	0.40	0.16	0.34	0.00
Ce(III)	0.14	0.00	0.42	0.20	0.90 0.00	0.80 0.00
Ce	-	-	0.40	0.20	0.00	0.00
La	1.00	0.81	0.46	0.25	1.00	0.55
In	0.86	0.63	0.87	0.63	0.72	0.40
Nb	0.00 0.27	0.00 0.00	0.82	0.00	0.60	0.00
Ca	-	-	0.62	0.31	0.00	0.00
Hf	0.00	0.00	0.70	0.00	0.00	0.00
Ti	0.00	0.00	0.66	0.00	0.10	0.00
Al	1.00	0.90	0.82	0.50	0.00	0.00

T A B L E IX
(Continued)

Cation	Solvents 9		10		11	
	R_L	R_T	R_L	R_T	R_L	R_T
Be	1.00	0.90	0.93	0.79	0.23	0.03
Ga	1.00	0.92	0.92	0.82	0.90	0.75
Pt	1.00	0.88	-	-	0.73	0.50
Se	0.34	0.00	1.00	0.00	0.36	0.00

Solvent systems used were:

(1) 0.1N Nitric acid

(2) Acetone + acetic acid + n-butanol + 4N HCl (1:1:1:1)

(3) n-Butanol + HCl (7:3)

(4) Ethylmethyl ketone + acetone + 50% HCl (7:3:1)

(5) Acetone + acetic acid + n-butanol + 1M NaCl (1:1:1:1)

(6) Acetone + acetic acid + n-butanol + 4N HNO_3 (1:1:1:1)

(7) 0.5N HCl + KCl saturated (1:1)

(8) Ethyl methyl ketone + acetone + 50% HCl (6:3:1)

(9) 1N H_3PO_4 + 1N HCl (1:1)

(10) Ethylmethyl ketone + acetone + 50% HCl (3:2:5)

(11) Ethylmethyl ketone + acetone + 50% HCl (1:6:1).

D I S C U S S I O N

A number of interesting points emerge from this study:

(a) The Rf values of metal ions are almost the same for the same developer whether the ion exchanger is stannic molybdate or stannic phosphate or stannic tungstate (6). This is clear from the Rf values given in table X.

T A B L E X

COMPARATIVE Rf VALUES OF SOME METAL IONS ON STANNIC MOLYBDATE (S.M.), STANNIC PHOSPHATE (S.P.) AND STANNIC TUNGSTATE (S.T.) PAPERS

Metal ion	Solvent system	Rf		Metal ion	Solvent system	Rf	
		S.M.	S.P.			S.M.	S.T.
Pb	n-Butanol + HCl(7:3)	0.12	0.02	Hg(I)	0.5N HCl + KCl satd. (1:1)	0.00	0.00
Cu		0.44	0.44	Hg		0.92	0.90
Fe		0.95	0.90	Ce(III)		0.87	0.82
Zn		0.74	0.77	Ce		0.00	0.03
Th		0.04	0.01	Pt		0.81	0.80
Al		0.12	0.07	Au		0.43	0.40
Be		0.40	0.38	Ir		0.07	0.00
UO_2		0.45	0.48	Y		0.90	0.82
Ni		0.14	0.13				
Mn		0.17	0.21				

(b) The papers show excellent selectivity when developed with mixed solvents. Any solvent is efficient enough to give some interesting separations.

(c) The results are reproducible and the preparation is easy and is not a difficult technique.

(d) Using only eleven solvents a number of interesting separations appear to be possible.

(i) Separation of Au from numerous metal ions using acetone + acetic acid + n-butanol + 4M HCl (1:1:1:1) as developer:

This separation is rapid and almost specific. Probably this is the best separation of gold yet reported. Even Sb and U which interfere in the method of Kember (7), do not interfere in this case.

(ii) Separation of Mg from numerous metal ions:

Mg can be separated from Ca, Sr, Ba, K, Rb, Cs, Y, Zr, Hf, Ce(III), Ti, La, Ni, Co, W, Te, Tl, Ag, Cr, Hg(I), UO_2, Mn and Cu using ethyl methyl ketone + acetone + 50% HCl (3:2:5) solvent system. The separation of Mg from Ca is particularly useful.

(iii) Separation of Rb from Cs: This separation is very neatly achieved using ethyl methyl ketone + acetone + 50% HCl (3:2:5) as developer. This is one of the most difficult separations and of all the separations reported in the literature this appears to be the best. The $\triangle$Rf is 0.5 which ensures a clean separation.

(iv) Al- Be - Ga . This separation is easily achieved in 3 hours using n-butanol + HCl (7:3) as mobile phase.

(v) Ga - Be, or Al, or Tl - In: This separation is achieved in 45 minutes using ethyl methyl ketone + acetone + 50% HCl (1:6:1) as solvent. It is possible that if longer development time is given Al - Be - Ga - In may be separated. However further study is needed before the full value of stannic molybdate papers can be assessed.

LITERATURE CITED

1. G. Alberti, F. Dobici and G. Grassini, J. Chromatog., 8, 103 (1962).

2. M.J. Nunes Da Costa and M.A.S. Jeronimo, ibid., 14 555 (1964).

3. G. Grassini and C. Padiglione, ibid., 13, 561 (1964).

4. M. Qureshi and S.Z. Qureshi, ibid., 22, 198 (1966).

5. M. Lederer, V. Moccatelli and C. Padiglione, ibid., 10, 456 (1961).

6. M. Qureshi, I. Akhtar and K.N. Mathur, Anal. Chem., 39, 1766 (1967).

7. N.F. Kember and R.A. Wells, Analyst, 76, 579 (1951).

C H A P T E R V

QUANTITATIVE SEPARATION OF IRON, ALUMINUM AND TITANIUM BY PAPER CHROMATOGRAPHY

Iron, aluminum and titanium are difficult to separate by classical means. Lacourt (1) developed a quantitative separation of iron, aluminum and titanium. Her separation suffers from many limitations: (i) iron and titanium are separated only if the sample is prepared in a particular manner, (ii) the method can not be used for varying ratios of iron, titanium and aluminum. Thus according to Macek: "when the samples are applied as solutions in 10% citric acid or in acetate buffer, all three cations are separated. When the cations are dissolved in dil. HCl or in dil. HNO_3, titanium and iron migrate as a single zone"(2). As a result her method has not gained wide acceptance. Paper chromatography was therefore undertaken to separate quantitatively iron, aluminum and titanium.

E X P E R I M E N T A L

Apparatus: Development was performed in 25 by 5 cm. glass jars employing the ascending technique. The dimension of the paper strip was 16 by 4 cm. Estimation was done on Bausch and Lomb Spectronic-20 (U.S.A.). All pH measurements were made on pH meter Model LI-10 (ELICO, Hyderabad, India). Whatman No. 1 paper was used for all quantitative work.

Reagents: Standard titanium solution containing 40 mg. Ti/ml was prepared by diluting analar grade titanic chloride solution with dilute hydrochloric acid and was standardized against ferric ammonium sulfate (3).

The stock solution of ferric ammonium sulfate containing 34.85 mg of Fe/ml was prepared in 5% sulfuric acid.

The stock solution of aluminum containing 8.537 mg. Al/ml was prepared in 1% H_2SO_4 and was standardized against EDTA (4).

The developer used was formic acid - hydrochloric acid - acetone in the ratio of (3:4:3). Titanium, iron, and aluminum were detected by 0.1% alcoholic alizarine Red-S.

Procedure: A mixture of titanium, iron and aluminum was applied on the line of application with the help of pipette. The strips were dried in air and saturated for fifteen minutes with the vapours of developer. The developer was allowed to ascend 12.5 cm. After drying the paper was detected. Pilot and blank were run simultaneously and were detected likewise. A 15% hydrochloric acid solution was used as blank. Separate zones for titanium, iron and aluminum were cut into small pieces. Titanium and aluminum were eluted separately thrice with 5% sulfuric acid taking 10 ml aliquot each time and heating on water bath for one hour. The eluting reagent for iron was 1% hydrochloric acid. These papers after elution were washed twice with 10 ml of distilled water and heating for fifteen minutes and the washings were mixed with the eluent. The final volume (50 ml) was reduced to 2-3 ml by evaporation on water bath. The paper pulp remaining in the container was oxidized by adding 2 ml. of the mixture of nitric acid and perchloric acid (1:3) + 2 ml of sulfuric acid. The solution was evaporated to 0.5-1 ml. The determination of titanium, iron and aluminum were done spectrophotometrically by sulfosalicylic acid (5); 1,10-phenanthroline (6); and eriochrome cyanine-R (7) respectively.

R E S U L T S

0.01 ml (10 λ) of a mixture of Ti(IV), Fe(III) and Al(III) was applied on the paper strips with the help of λ-pipette. The zones of Ti, Fe and Al were cut, eluted and determined spectrophotometrically. The results are summarised in table XI.

T A B L E XI

DETERMINATION OF Fe^{+3}, Al^{+3} AND Ti^{+4}

Ti^{+4} applied (μg)	Ti^{+4} recovered (μg)	% Error	Fe^{+3} applied (μg)	Fe^{+3} recovered (μg)	%Effor	Al^{+3} applied (μg)	Al^{+3} recovered (μg)	%Error
133.3	133.3	0.0	23.2	23.1	- 0.4	28.0	27.0	- 3.0
133.3	133.3	0.0	23.2	23.1	- 0.4	28.0	29.0	+ 3.0
133.3	133.3	0.0	11.46	11.5	+ 0.3	28.0	27.0	- 3.0
133.3	133.3	0.0	11.46	11.5	+ 0.3	28.0	26.5	- 4.5
133.3	133.3	0.0	11.46	11.5	+ 0.3	28.0	28.0	± 0.0

D I S C U S S I O N

Considering the large number of separations reported by paper chromatography it is surprising that Fe-Ti-Al have been separated by a very few workers. Probably only Lacourt has studied the quantitative aspects of this separation. The method of separation described here is better than that of Lacourt in the following aspects:

(i) No special method is necessary for the preparation of the sample.

(ii) None of the common cations affect this separation except those which precipitate the metals. Even then the precipitate may be dissolved in a complexing agent i.e. tartrate etc. and the chromatography can be performed as usual.

(iii) The highly acidic medium ensures that the anions of weak acids are present in the acid forms and hence such anions as tartrate, citrate, which are expected to interfere in the common chromatographic separations do not interfere in this case.

LITERATURE CITED

1. A. Lacourt, GH. Sommereyns and G. Wantier, "Proceedings of the International Congress on Analytical Chemistry, Oxford, England", pp. 387-97, (1952).

2. I.M. Hais and K. Macek, "Paper Chromatography, A comprehensive treatise", III Edition, Academic Press, New York and Publishing house of the Czechoslov. Acad. of Sciences, Prague, 873 (1963).

3. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Part II, Vol. 5, Interscience Publishers, New York - London, pp. 49-51 (1961).

4. P.J. Welcher, "The Analytical uses of Ethylene diamine tetraacetic acid", II Edn. D. Van. Nostrand, Co., Inc. Princeton, N.J., New York, pp. 165-66 (1958).

5. M. Ziegler and O. Glemser, Z. anal. Chem., 139, 92 (1953).

6. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd (revised ed.), Interscience Publishers, Inc., New York, p. 541 (1959).

7. W.E. Thrun, Anal. Chem., 20, 1117 (1948).

C H A P T E R VI

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM WITH SULFOSALICYLIC ACID

Very few spectrophotometric methods are available for the determination of titanium which are sensitive and free from interferences. Ziegler (1) used the yellow color with sulfosalicylic acid for the determination of titanium. According to Sandell (2), "An attractive feature of this method is the noninterference of common metals: aluminum, manganese, calcium, magnesium, and iron. The effect of less common elements requires investigations". The sulfosalicylic acid method was therefore investigated in detail with regard to the proper wavelength, the interferences of common anions, less common cations; and effect of temperature. The possible masking of interfering ions has also been studied.

E X P E R I M E N T A L

Apparatus: Spectrophotometric studies were performed on Bausch and Lomb Spectronic-20. pH measurements were done on pH meter model LI-10 (ELICO, Pvt. Ltd. Hyderabad, India).

Reagents: Standard titanium solution was prepared by dissolving 1.00 gram of titanium dioxide in 100 ml. of concentrated sulfuric acid containing 50 grams of ammonium sulfate and diluted to a liter. The resulting solution contained 0.5995 mg. titanium per ml. It was standardized with ferric alum (3). To ten millilitere of this were added 10 ml sulfuric acid and 5 gms. of ammonium sulfate. It was then diluted to 100 ml with distilled water.

Acetate buffer was prepared by dissolving 6.5 grams of sodium acetate and 10.5 ml of glacial acetic acid in water and making it to one liter, pH was 4.

A 20% sulfosalicylic acid solution was prepared by dissolving the required amount of sulfosalicylic acid in water and the solution was filtered if it was not clear.

5% Ferric chloride solution was prepared by dissolving 5 grams of ferric chloride in water and 8 - 10 drops of

concentrated hydrochloric acid were added to check the hydrolysis.

All the chemicals were of reagent grade.

Procedure: Take 5 - 10 ml of titanium solution slightly acidic, (5-100 μg of Ti) in a 50 ml volumetric flask. Add 5 ml of 20% sulfosalicylic acid and one drop of 5% ferric chloride solution. Then add ammonia until the color changes to yellow, followed by 20 ml of buffer solution. Mix add 5 ml of fresh 4% merceptoacetic acid solution and dilute to 50 ml by water. After 10 minutes take the absorbance at 355 mμ against the blank. The color is stable and is proportional to titanium concentration.

R E S U L T S

Spectrum of titanium sulfosalicylic acid complex:

Applying the above procedure for a solution containing 60 μg of titanium, the absorbance was taken at various wavelengths (325 - 650 mμ.) and the results are plotted in figure 9.

The maximum occurs at 355 m μ .

Time versus absorbance studies showed that no significant change occurs upto 20 hours (figure 10).

pH versus absorbance studies were also made and it was found that color intensity remains constant from pH 3 to 5.5 (figure 11).

Calibration Curve: Absorbance of the solutions containing 0 - 120 μg of titanium were taken at 355 m μ . Absorbance Vs. concentration were plotted, which is a straight line (figure 12).

Effect of temperature: The color is stable from 0°C -100°C and there is only a very slight decrease in absorbance (figure 13).

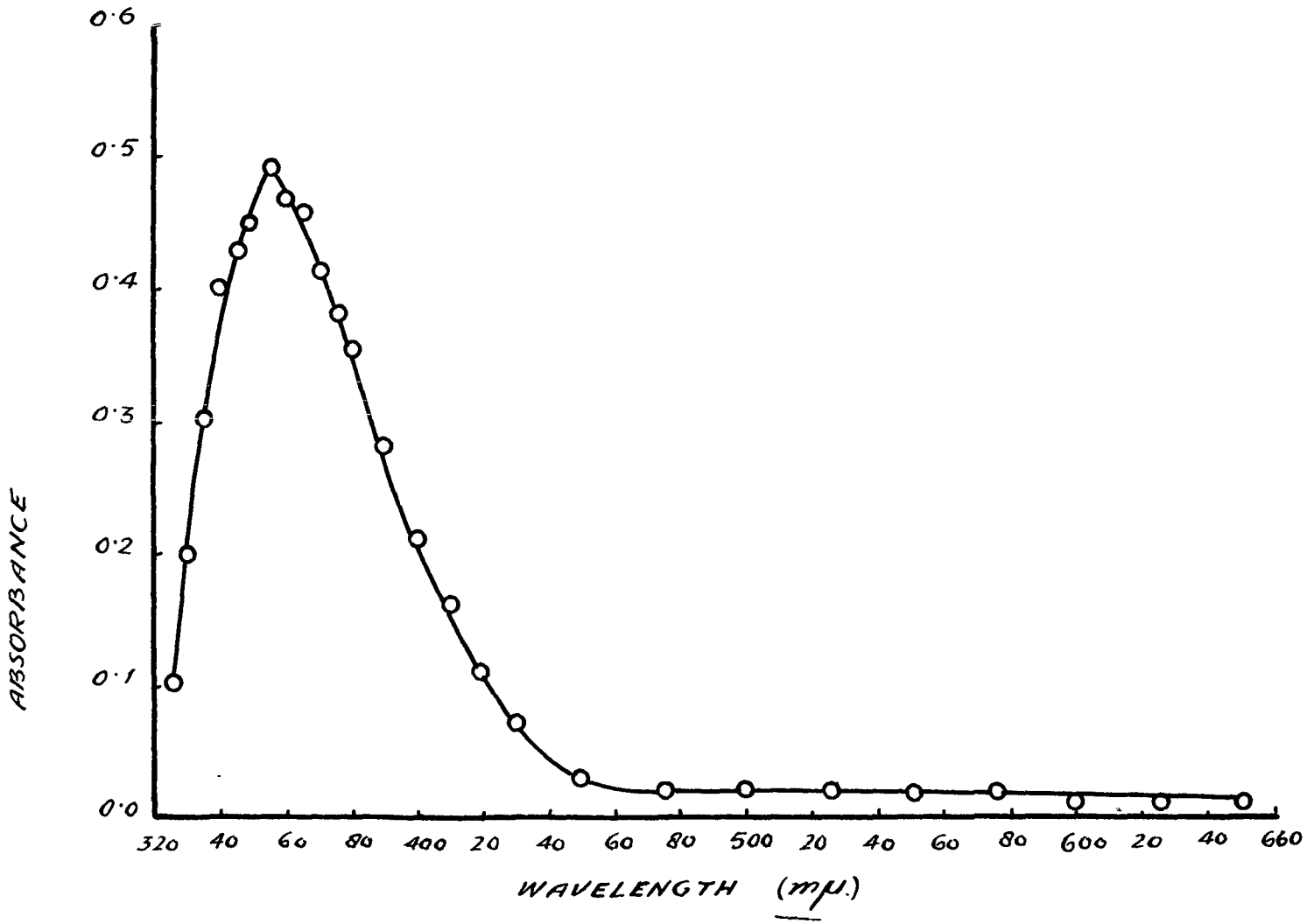


FIG. 9. SPECTRUM OF TITANIUM SULFOSALICYLIC ACID COMPLEX

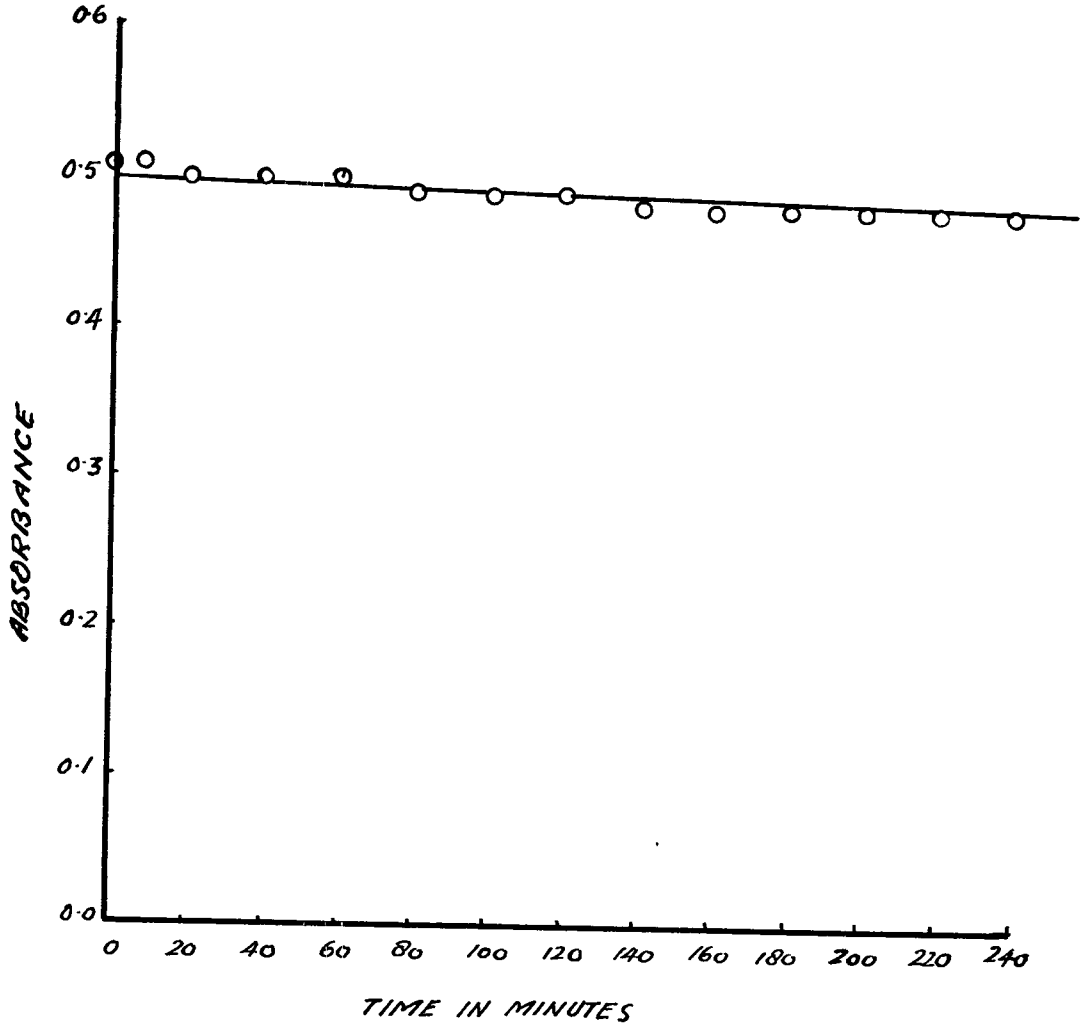


FIG. 10. ABSORBANCE vs TIME FOR TITANIUM-SULFOSALICYLIC ACID COMPLEX AT 355 mμ.

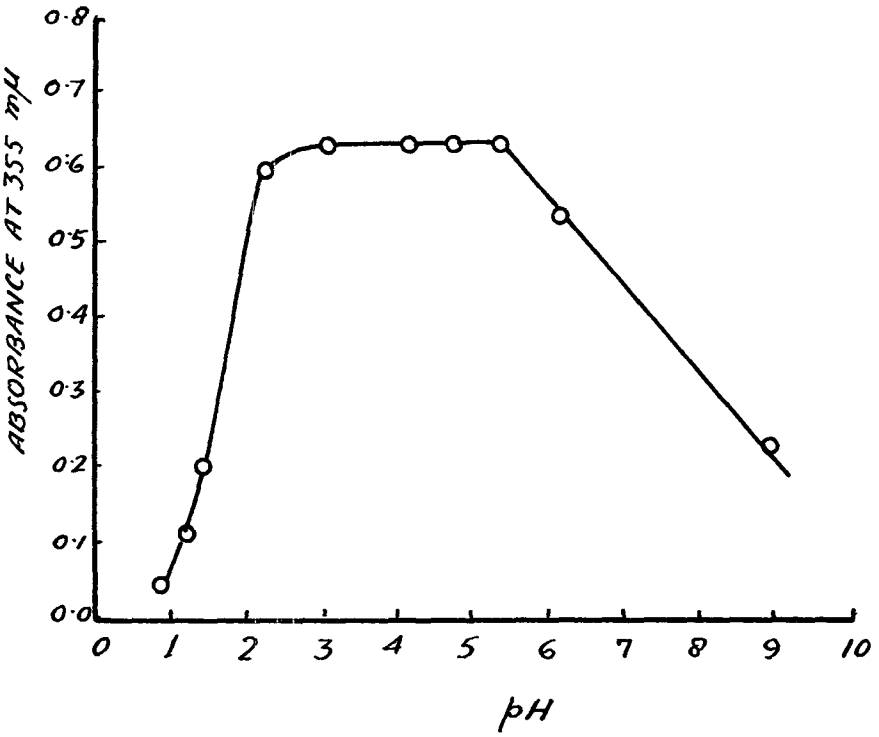


FIG. 11. EFFECT OF pH ON Ti-SULFOSALICYLIC ACID COMPLEX

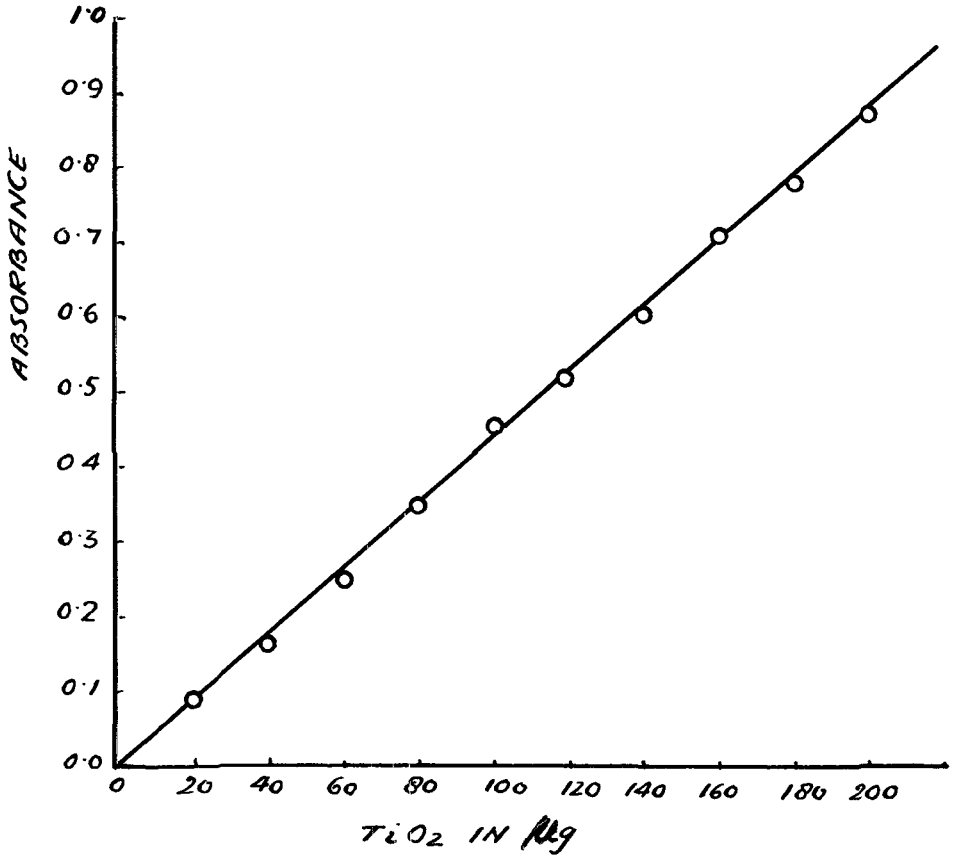


FIG. 12. CALIBRATION CURVE OF TITANIUM SULFOSALICYLIC ACID COMPLEX AT 355 mμ

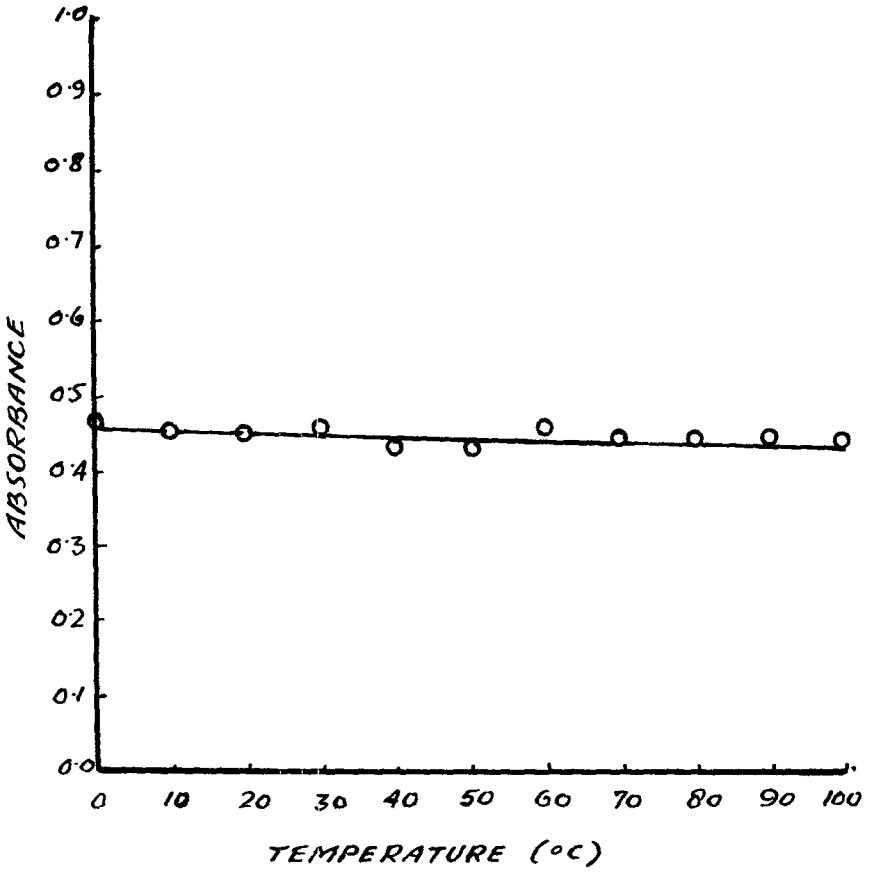


FIG. 13. ABSORBANCE VS TEMPERATURE FOR TITANIUM-SULFOSALICYLIC ACID COMPLEX AT 355 mμ.

Effect of foreign ions: The influence of foreign ions on titanium was determined; following ions do not interfere when present in hundred fold excess: Al, Mn, Ca, Mg, Zn, Th, Zr, La, Sn, Ce, Tl (ous), In, Ni, Cd, Hg(II), Y(III), NH_4(I), Ce(III), S^{-2}, $CN^{'}$, $Cl^{'}$, $I^{'}$, $Br^{'}$, SO_4^{-2}, AsO_4^{-3}, arsenite, formate, chlorate, oxalate, iodate, thiocyanate, nitrate. The results are summarized in table XII. Ions which interfere in 100 fold excess in the above procedure are: Bi, Ce(IV), Co, Cr, Cu, Mo, Pd, Pt, Te, U, V, W, citrate, tartrate, $S_2O_3^{-2}$, $F^{'}$.

Removal of interferences: Pd was masked by adding 10 drops of 10% KCN before adding sulfosalicylic acid to the above procedure. The interference of Co, Pt, Bi, Pd, and Cu was removed if 5% ascorbic acid was used in place of mercaptoacetic acid. The precipitate obtained in the case of Pt, Pd, Bi and Cu was removed by centrifuging before making the solution upto 50 ml. The results are summarized in table XIII.

T A B L E XII

EFFECT OF FOREIGN IONS ON TITANIUM DETERMINATION AT 355 mμ.

Titanium solution taken = 100 μg of TiO_2

S.No.	Impurity added 6000 μg of	TiO_2 found μg	% Error
1.	Al(III)	100	± 0.00
2.	Mn(II)	98	- 2.0
3.	Ca(II)	100	± 0.0
4.	Mg(II)	98	- 2.0
5.	Zn(II)	98.5	- 1.5
6.	Th(IV)	100	± 0.00
7.	Zr(IV)	104	+ 4.0
8.	La(III)	100.5	+ 0.5
9.	Sn(IV)	97	- 3.0
10.	Sn(II)	99	- 1.0
11.	Ga(III)	93.5	- 6.5
12.	Tl(I)	96	- 4.0
13.	In(III)	95	- 5.0
14.	Ni(II)	108	+ 8.0
15.	Cd(II)	102.5	+ 2.5
16.	Hg(II)	101	+ 1.0
17.	Y(III)	99	- 1.0
18.	NH_4(I)	105	+ 5.0

T 711

T A B L E XII
(Continued)

S.No.	Impurity added 6000 μg of	TiO_2 found μg	% Error
19.	Ce(III)	101	+ 1.0
20.	CN^-	101.5	+ 1.5
21.	arsenate	104	+ 4.0
22.	arsenite	103	+ 3.0
23.	Sulfide	96	- 4.0
24.	formate	102	+ 2.0
25.	I'	98	- 2.0
26.	Br'	100	± 0.00
27.	ClO_3'	102	+ 2.0
28.	$C_2O_4^{-2}$	102	+ 2.0
29.	IO_3'	98	- 2.0
30.	SO_3^{-2}	94	- 6.0
31.	Cl'	100	± 0.00
32.	BrO_3'	97	- 3.0
33.	SO_4^{-2}	100	± 0.00
34.	Acetate	100	± 0.00
35.	NO_3'	100	± 0.00

T A B L E XIII

DETERMINATION OF TITANIUM USING ASCORBIC ACID AT 355 mμ.

TiO_2 taken = 100μg.

S.No.	Impurity added 6000μg of	TiO_2 found μg	% Error
1.	Co(II)	98	- 2.0
2.	Pt(IV)	100	± 0.00
3.	Pd(II)	101	+ 1.0
4.	Cu(II)	100	± 0.0

D I S C U S S I O N

The present study shows that in the sulfosalicylic acid method even the less common ions like: Th, Zr, La, Ga, Tl, In, Y, and Cs do not interfere in addition to the ions mentioned by Ziegler (1). Interference due to metal ions like Co(II), Pt(IV), Pd(II) and Cu(II) is completely removed when ascorbic acid is used in place of mercapto-acetic acid. Further 0.5 ml 10% KCN when added before adding sulfosalicylic acid easily masks 6000 μg of Pd and 100 μg of TiO_2 is accurately determined under these conditions and no separation is required. Out of the various anions tried only tartrate, citrate, fluoride and thio-sulfate interfere. The method is therefore highly selective for the determination of titanium. Further when the determination is performed at 355 mμ instead of 445 mμ the method becomes ten times more sensitive. Since now 355 mμ lies on the plateau the method should also be more precise. It therefore appears that this is probably the best method for the determination of titanium.

LITERATURE CITED

1. W. Ziegler and O. Glemser, Z. anal. Chem., 139, 92 (1953).

2. E.B. Sandell, "Colorimetric Determination of Traces of Metals", Third Edition, (revised and enlarged), Interscience Publishers, Inc., New York, p. 876 (1959).

3. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Part II, Vol. 5, Interscience Publishers, New York, London, p. 49 (1961).

C H A P T E R VII

DETERMINATION OF LEAD IN PRESENCE OF BARIUM WITH POTASSIUM FERROCYANIDE USING DEAD STOP TECHNIQUE

There is renewed interest in dead stop titrations of metal ions with potassium ferrocyanide owing to their ease and simplicity. Zinc (1), gallium (2), indium (3), and thallium (4) have been successfully titrated. The present investigation was taken up to assess the utility of potassium ferrocyanide as a titrant for lead. As a result it has been found that precise accurate and reproducible results can be obtained using this method for the determination of lead in the presence of ten times of barium.

E X P E R I M E N T A L

Reagents: All reagents were either E. Merck (Darmstadt) or B.D.H. (Analar). Lead acetate and lead nitrate solutions were prepared by standardizing with E.D.T.A. (5). A few drops of glacial acetic acid were added to the lead acetate solution till it became clear. Potassium ferrocyanide was standardized by titration against zinc(6). It was preserved using the usual precautions (7,4) to check decomposition.

Apparatus: The electrical arrangement used was the same as that of Foulk and Bawden (8).

Method: Five to ten ml of lead nitrate or acetate solution were taken in a 250 ml. beaker and diluted to nearly 60 - 80 ml with water so as to dip the platinum electrodes in the solution completely. Potassium ferrocyanide was added to it and the deflection for each addition was recorded. The end point was detected by the break in the curve of current vs. volume of titrant.

R E S U L T S

The results for the titration of lead nitrate (0.084M) with 0.0503N potassium ferrocyanide at 600 mv. are summarized in table XIV.

T A B L E XIV

DEAD STOP TITRATION OF LEAD NITRATE WITH POTASSIUM FERROCYANIDE AT 600 mv.

S.No.	Moles of Pb(II)	Moles of $Fe(CN)_6^{-4}$	Mole ratio $Fe(CN)_6^{-4}$: Pb(II)
	x 10^{-4}	x 10^{-4}	
1	4.20	2.012	1 : 2.087
2	4.20	2.0623	1 : 2.036
3	4.20	2.0623	1 : 2.036
4	4.20	2.0623	1 : 2.036
5	4.20	2.0623	1 : 2.036
6	4.20	2.1126	1 : 1.988
7	8.40	4.224	1 : 1.988
8	5.88	2.917	1 : 1.989
9	5.04	2.515	1 : 2.003

Average mole ratio = 1:2.022
Standard deviation = 0.0312

In order to study the effect of anions on this titration a few titrations were also performed using lead acetate. 5 ml. of 0.098M lead acetate required 4.900 ml of 0.0503M potassium ferrocyanide.

The titration was also performed in the presence of barium. The results are summarized in figure (14c).

To find out the best potential for this titration, it was performed at 0.3, 0.4, 0.5, 0.6 and 0.75 volts (Figure 15). It was noticed that the end point could be accurately determined at any one of these potentials but best results were obtained when the potential was from 0.5 - 0.75 volts.

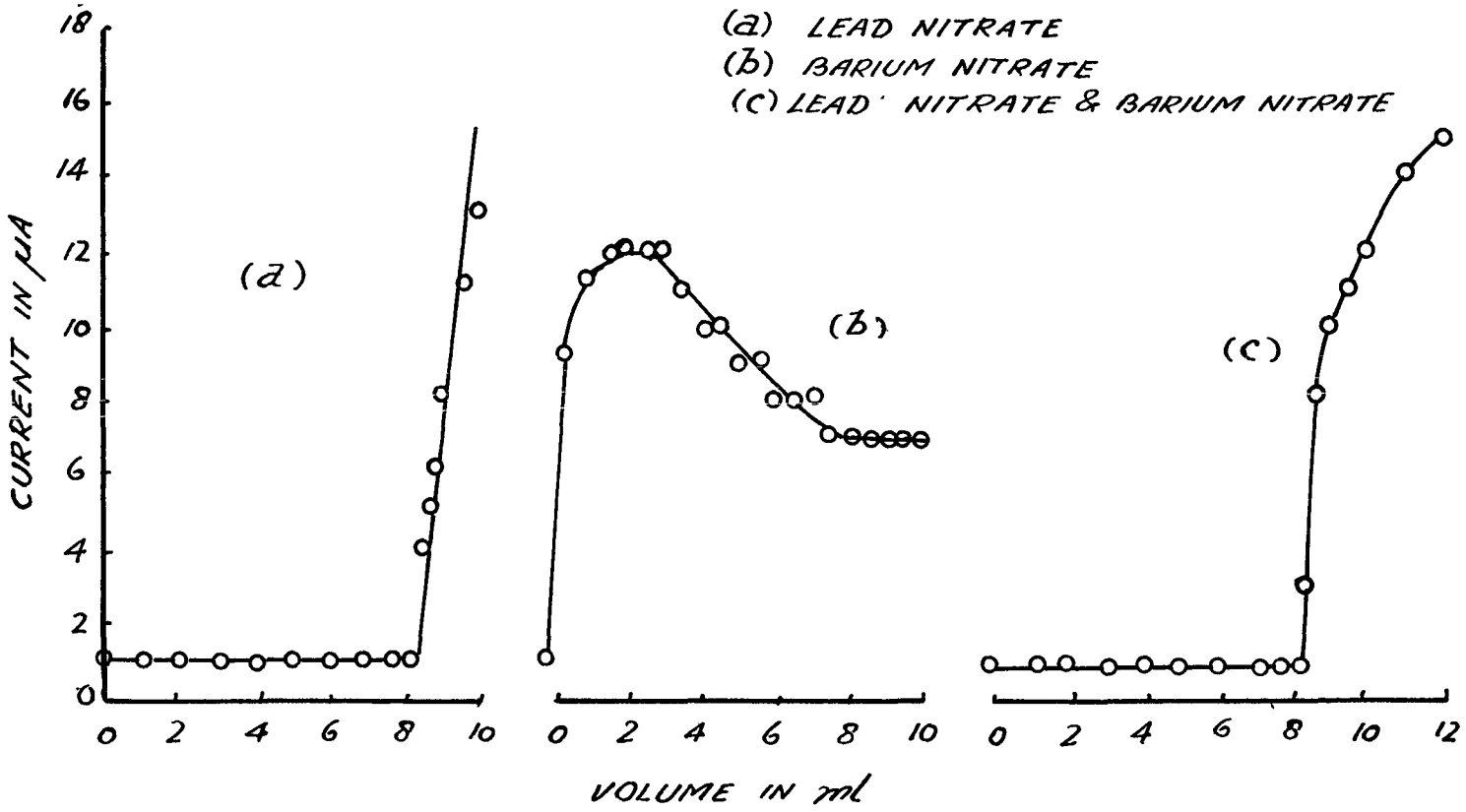
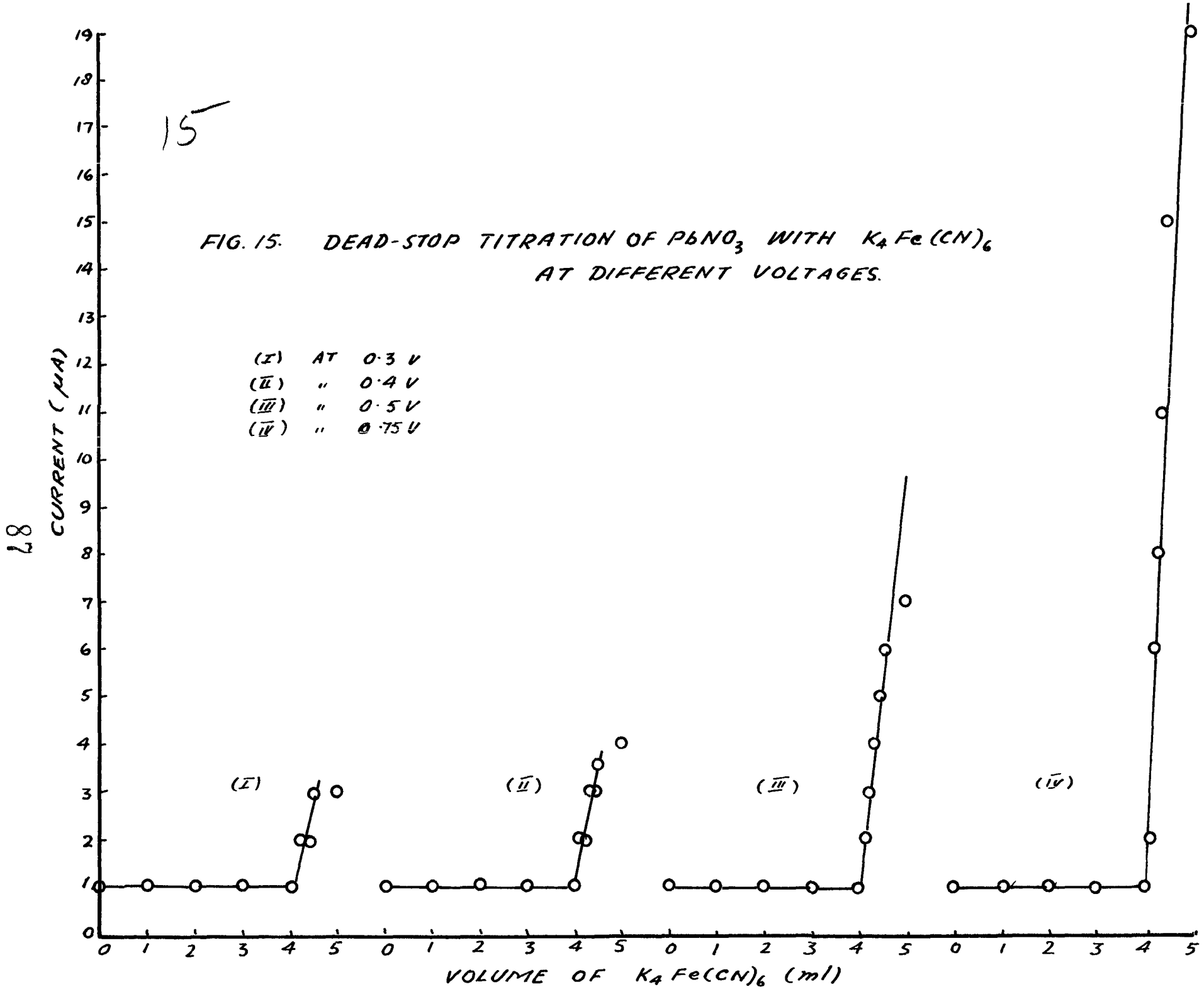


FIG. 14 DEAD STOP TITRATION WITH POTASSIUM HEXACYANOFERRATE (II)

FIG. 15. DEAD-STOP TITRATION OF $PbNO_3$ WITH $K_4Fe(CN)_6$ AT DIFFERENT VOLTAGES.



D I S C U S S I O N

The results show that lead can be determined either as nitrate or as acetate accurately using the dead-stop method. The shape of the curve (14a) resembles the curve for the titration curve for the titration of an irreversible system with a reversible system. At the potential used in this case the reduction of lead (II) is irreversible while the reduction of ferricyanide is reversible. Hence when all lead has been precipitated there is an excess of ferrocyanide, which contains a small quantity of ferricyanide and a sharp rise in current is noticed. Since barium ferrocyanide is much more soluble than the lead salt, hence lead ferrocyanide is precipitated first. As soon as lead ferrocyanide has been completely precipitated a little excess of ferrocyanide may be present as ferrocyanide or as barium ferrocyanide. In both cases an increase in current is expected since barium ferrocyanide due to its fair solubility will provide sufficient ferrocyanide ions. This explanation is in consonance with the curves in figure 14. In 14(b) the current increases from the very beginning owing to the solubility of barium ferrocyanide. In 14(c) after the end point the increase in

current is not as sharp as in 14(a) since some ferrocyanide has been tied up as barium ferrocyanide.

LITERATURE CITED

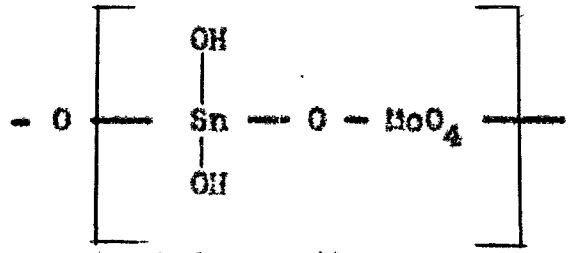
1. D.P. Swinehart, Anal. Chem., 23, 380 (1951).
2. N.R. Fetter and D.P. Swinehart, ibid., 28, 122 (1956).
3. L.S. Martens and H. Frye, ibid., 35, 969 (1963).
4. R.B. Williams and H. Frye, ibid., 36, 945 (1964).
5. F.J. Welcher, "The Analytical uses of Ethylene Diamine Tetraacetic Acid", D. Van Nostrand Co. Inc. N.J. p. 189 (1958).
6. I.M. Kolthoff and E.B. Sandell, "Text Book of Quantitative Inorganic Analysis". The Macmillan Co. New York, III Edn., pp. 549-51 (1959).
7. Ibid, p. 563.
8. C.W. Foulk and A.T. Bawden, J. Am. Chem. Soc., 48, 2045 (1926).

S U M M A R Y

The present work describes (a) Preparation and properties of stannic molybdate (b) Chromatography of metal ions on stannic molybdate papers (c) Detection of ferrous ions with stannic molybdate (d) Quantitative separation of Fe, Al and Ti by paper chromatography (e) Spectrophotometric determination of titanium using sulfosalicylic acid (f) Dead-stop titration of lead with potassium ferrocyanide in the presence of barium.

Stannic molybdate has been prepared by mixing aqueous 0.02M stannic chloride and 0.05M ammonium molybdate in a molar ratio of (1:2). The composition of the gel has been established using classical volumetric and gravimetric methods. It has been found to be Sn:Mo (1:1). High frequency studies however showed an apparent combining ratio of Sn:Mo (1:2). The ion exchange capacity of this ion exchanger has been found to be 0.92 to 1.04 for Na, K, Ba and Mg ions. The ion exchanger is stable in nitric, sulfuric, acetic and formic acids of all concentrations. 0.5N HCl and 60% perchloric acid have also no effect on

the ion exchanger in three days. The solubility of stannic molybdate in water and 6M HNO_3 was also quantitatively determined. The pH titration curve for this ion exchanger shows only one inflection point corresponding to monofunctional acidic group. X-Ray diffraction showed that the material is non crystalline. K_d values for 12 common cations were also determined for this ion exchanger. The structure of this substance is tentatively proposed as



Thermogravimetric studies were performed and the results discussed in the light of the structure proposed above.

Stannic molybdate gel was crushed and sieved and the beads so obtained were used for the specific detection of ferrous ions using the following procedure:

To one ml of the unknown solution, approx. 0.1M $Hg_2(NO_3)_2$ was added dropwise. If a precipitate appeared then addition of mercurous nitrate was continued till complete precipitation. The precipitate was filtered and to the filtrate ammonium acetate 1M aqueous solution was added. Any precipitate which appeared was filtered. To this filtrate were added a few beads of the exchanger stannic molybdate. The beads

turned black in presence of ferrous ions.

This test has been found to be specific for ferrous ions. The interference of Ti^{+3} and Sn^{+2} is completely removed by the mercurous nitrate treatment which oxidises Ti^{+3} and Sn^{+2} to Ti^{+4} and Sn^{+4} ions respectively. The color produced when the ion exchanger reacts with various organic materials has also been studied and it is possible to develop some new tests on the basis of this test.

Papers impregnated with stannic molybdate have been prepared and 47 cations have been chromatographed in the following solvent systems:

(1) 1.0N HNO_3

(2) Acetone + acetic acid + n-butanol + 4N HCl (1:1:1:1)

(3) n-Butanol + HCl (7:3).

(4) Ethyl methyl ketone + acetone + 50% HCl (7:3:1)

(5) Acetone + acetic acid + n-butanol + 1N NaCl (1:1:1:1)

(6) Acetone + acetic acid + n-butanol + 4N HNO_3 (1:1:1:1).

(7) 0.5 HCl + satd. aq. KCl (1:1).

(8) Ethyl methyl ketone + acetone + 50% HCl (6:3:1).

(9) 1M H_3PO_4 + 1N HCl (1:1).

(10) Ethyl methyl ketone + acetone + 50% HCl (3:2:5).

(11) Ethyl methyl ketone + acetone + 50% HCl (1:6:1).

As a result of this study a number of useful

separations appear to be possible. Some of which are given below:

T A B L E I

Separation of	Solvent system No.	R_f values	
		Cation separated	Other ions
Ga from numerous metal ions.	3	Ga(1.00-0.91)	less than 0.50
Au from numerous metal ions	2 or 6	Au(1.0 -0.73)	less than 0.70
	6	Au(1.0 -0.86)	less than 0.65
Mg from numerous metal ions	10	Mg(1.00-0.90)	less than 0.70
Al-Be-Ga	3	Ga(1.00-0.91)	Be(0.40) Al(0.12)
Ga-In-Tl	3	Ga(1.00-0.91)	In(0.38) Tl(0.00)

Quantitative aspects of the separation of Fe - Al - Ti have been studied. The mixture is separated by using the developer HCl + HCOOH + CH_3-CO-CH_3 (4:3:3). Titanium, iron and aluminum spots after separation were eluted and determined with sulfosalicylic acid, 1,10-phenanthroline and eriochrome cyanine-R respectively. The 3 ions were quantitatively separated. Ziegler's method for the spectrophotometric determination of titanium with sulfosalicylic acid has been re-examined. It has been found that the determination

is more sensitive at 355 mμ instead of 445 mμ as proposed by Ziegler and Clemser. The interference due to Co, Pt and Cu is completely removed by using ascorbic acid in place of mercaptoacetic acid. Less common ions: Th, Zr, La, Ga, Tl, In, Y and Ce have been found not to interfere in this method.

Lead has been determined in the presence of barium by the dead-stop technique using potassium ferrocyanide as the titrant. Best results were obtained when the potential was from 0.50 to 0.75 volts. Lead can be accurately determined in the presence of 10 times of barium by this technique.